PB-227 058

REDUCTION OF ATMOSPHERIC POLLUTION BY THE APPLICATION OF FLUIDIZED-BED COMBUSTION AND REGENERATION OF SULFUR-CONTAINING ADDITIVES

G. J. Vogel, et al

Argonne National Laboratory

Prepared for:

Environmental Protection Agency

June 1973

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5285 Port Royal Road, Springfield Va. 22151

73

BIBLIOGRAPHIC DATA SHEET	1. Report No. EPA-R2-73-253	2.	PB 227 058

4. Title and Subtitle
Reduction of Atmospheric Pollution by the Application of Fluidized-Bed Combustion and Regeneration of Sulfur-Containing Additives

5. Report Date
June 1973

6.

7. Author(s) G. J. Vogel, E. L. Carls, J. Ackerman, M. Haas, J. Riha, C. B. Schoffstoll, J. Hepperly, and A. A. Jonke

8. Performing Organization Rept. No. ANL/ES-CEN-1005

9. Performing Organization Name and Address
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

10. Project/Task/Work Unit No.

11. Contract/Grant No.
EPA-IAG-0020

12. Sponsoring Organization Name and Address
EPA, Office of Research and Monitoring
NERC/RTP, Control Systems Laboratory
Research Triangle Park, North Carolina 27711

13. Type of Report & Period Covered Annual
July 1971-June 1972

14.

15. Supplementary Notes

16. Abstracts

The report discusses fluidized-bed combustion (FBC) as a means of removing from the gas phase nearly all of the atmospheric pollutants (sulfur and nitrogen compounds) generated during the combustion of fossil fuels. Particulate lime solids (additives) are introduced into the fluidized bed and react with the sulfur compound formed during combustion. It discusses: pollution control by FBC of oil with an excess of air and by the combustion of coal with a deficiency of air; the thermodynamics of several proposed processes for regenerating additives; and regeneration of sulfur-containing additive by the two most promising processes--a one-step reductive decomposition of $CaSO_4$ and a two-step (reduction-CO_2/H_2O regeneration) procedure.

17. Key Words and Document Analysis. 17a. Descriptors

Air Pollution
Fluidized-Bed Processing
Sulfur Oxides
Nitrogen Oxides
Limestone
Dolomite (Rock)
Combustion
Oils
Coal
Calcium Sulfates
Sulfur
Additives
Fossil Fuels
Calcium Oxides
Stoichiometry
Thermodynamics

17b. Identifiers/Open-Ended Terms

Air Pollution Control
Stationary Sources
Fluidized-Bed Combustion
Fluidized-Bed Oil Combustion
Two-Stage Coal Combustion

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NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

17c. COSATI Field/Group 13B

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages
Unlimited	UNCLASSIFIED	73 74
	20. Security Class (This Page) UNCLASSIFIED	22. Price 6.75

EPA-R2-73-253

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Argonne No. ANL/ES-CEN-1005

Interagency Agreement EPA-IAG-0020
Program Element No. 1A2013

EPA Project Officer: D.B. Henschel

Control Systems Laboratory
National Environmental Research Center
Research Triangle Park, North Carolina 27711

Prepared for

OFFICE OF RESEARCH AND MONITORING
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

June 1973

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

TABLE OF CONTENTS

		Page
ABSTRACT		7
I.	SUMMARY	7
II.	INTRODUCTION	14
III.	BENCH-SCALE, ATMOSPHERIC COMBUSTION EXPERIMENTS	16
	A. Materials	16
	1. Coal	16
	2. Oil	16
	3. Additives	16
	4. Starting Bed Material	16
	B. Equipment and Procedure	16
	C. Results and Discussion	19
	1. Air-Deficient Coal Combustion Experiments	19
	2. Oil Combustion Experiments with an Excess of Oxygen	27
	3. Cyclone Collection Efficiencies during Coal Combustion Experiments	32
	4. Combustion Efficiencies for Coal, Oil, and Natural Gas Combustion with Excess Air	32
IV.	REGENERATION OF SULFUR-CONTAINING ADDITIVES	34
	A. Thermodynamic Analysis of Some Schemes for Regenerating Partially Spent Additive from the Fluidized-Bed Combustion of Coal	34
	1. Thermal Decomposition of Calcium Sulfate	35
	2. Reductive Decomposition of Calcium Sulfate	38
	3. Roasting of Calcium Sulfide	45
	4. Pressure Effects in the CO/CO_2 and H_2/H_2O Systems	48
	5. Acid-Base Reaction of Calcium Sulfide with H_2O and CO_2	48
	B. Experimental Studies	51
	1. Reductive Decomposition of $CaSO_4$	51
	2. Two-Step Process	52
V.	PRESSURIZED COMBUSTION AND REGENERATION PILOT PLANT	64
	A. Description	64
	B. Petrocarb Solids Feeder Tests	69
VI.	ACKNOWLEDGMENTS	72
VII.	REFERENCES	72

LIST OF FIGURES

No.	Title	Page
1	Simplified Equipment Flowsheet of Atmospheric Bench-Scale Fluidized-Bed Combustor and Associated Equipment	18
2	Equipment for Feeding Oil to the 6-in.-dia Combustor	20
3	Effect of Air Feed Rate on Percent of Sulfur in Off-Gas as H_2S	22
4	Sulfur Retention in Oxygen-Excess and Oxygen-Deficient Experiments.	24
5	Effect on Sulfur Retention of Air Feed Rate to First Stage	24
6	Effect of Air Feed Rate and Fluidized-Bed Temperature on NO Concentration in Off-Gas from the First Stage During Combustion of Coal	24
7	Effect of Temperature on Sulfur Retention during Combustion of Residual Fuel Oil in Excess Air	29
8	Effect of Ca/S Mole Ratio on Sulfur Retention during Combustion of Residual Fuel Oil in Excess Air.	30
9	Pressure of SO_2 in Equilibrium with CO/CO_2 Mixtures as a Function of Temperature.	39
10	Temperature and CO/CO_2 Conditions for Formation of $CaSO_4$, $CaSO_3$, and CaS	40
11	Equilibrium Dissociation Pressure of $CaCO_3$ as a Function of Temperature.	41
12	S_2 and COS Concentrations at Equilibrium as a Function of Temperature and CO/CO_2 Ratio	44
13	Pressure of SO_2 in the $CaSO_4$-CaS-H_2-H_2O System	46
14	S_2 and H_2S Pressures in the System S_2-H_2S-H_2-H_2O-$CaSO_4$-CaS	47
15	Equilibrium Constant as a Function of Temperature $CO_2 + H_2O + CaS \rightarrow CaCO_3 + H_2S$.	49
16	Pressure of H_2S in Undried Gas Stream as a Function of Temperature at 10-atm P_{total}	49
17	Schematic of Apparatus for Equilibrium Measurements on $CaSO_4$-CO/CO_2 System.	51
18	Experimental and Calculated Partial Pressures of SO_2 Over a Range of P_{CO}/P_{CO_2} Ratios	53

No.	Title	Page
19	Two-Inch-Diameter Fluidized-Bed Reactor.	54
20	Sulfide Content of Bed During Reduction of Partially Sulfated Dolomite with Hydrogen at Various Temperatures. . . .	55
21	Effect of Temperature on Reduction of $CaSO_4$.	55
22	Typical H_2S Levels in the Outlet Gas for CO_2/H_2O Regeneration.	56
23	H_2S Concentration in Effluent Gas Stream in Regeneration Step.	59
24	Photomicrograph Showing Cross Sections of Particles from Cyclic Experiment X100	62
25	Photomicrograph Showing Cross Sections of Particles from Cyclic Experiment X100	63
26	Simplified Schematic of Pressurized Combustion-Regeneration Equipment.	64
27	Six-inch Fluidizing Gas Preheater.	65
28	Six-inch Dia Pressurized Fluidized-Bed Combustor	66
29	Three-inch Dia Fluidized-Bed Regenerator	68
30	Model 16 ABC Petrocarb Injector.	70
31	Cross Section of Mixing Valve Assembly	71

LIST OF TABLES

No.	Title	Page
1	Some Chemical and Physical Characteristics of Coal from Fourth Shipment from Commonwealth Edison Co.	17
2	Properties of Esso Residual Fuel Oil Used in Combustion Experiments.	17
3	Carbon Balances and Carbon Contents of Solids in Coal Combustion Experiments with a Deficiency of Air.	26
4	Operating Data and Results, Combustion of Residual Fuel Oil in Excess Air.	28
5	Particle Size Distributions and Bulk Densities for Solids Samples from Experiment OIL-3C	32
6	ΔG°_{f}, Free Energy of Formation	36
7	Pressure of SO_3 and SO_2 in Equilibrium with CaSO	38
8	H_2S Concentration in Dried and Undried Product Gas Stream at Equilibrium	50
9	Regeneration Experiment, Conditions and Results.	57
10	Conditions for Cyclic Experiment	60
11	Sieve Size Analysis of Starting Bed and Final Bed After Six Cycles	63

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ABSTRACT

Fluidized-bed combustion is being studied as a means of removing from the gas phase nearly all of the atmospheric pollutants (sulfur and nitrogen compounds) generated during the combustion of fossil fuels. Particulate lime solids (additives) are introduced into the fluidized bed and react with the sulfur compound formed during combustion. Information has been obtained on (1) pollution control by fluidized-bed combustion of oil with an excess of air and by the combustion of coal with a deficiency of air, (2) the thermodynamics of several proposed processes for regenerating additives, and (3) experimental regeneration of sulfur-containing additive by the two most promising processes--a one-step reductive decomposition of $CaSO_4$ and a two-step (reduction-CO_2/H_2O regeneration) procedure.

I. SUMMARY

Argonne National Laboratory is investigating pollution control aspects of fluidized-bed combustion in a program funded by the Control Systems Division of the Environmental Protection Agency. The program consists of investigating (1) the effects of operating variables in reducing pollutant emissions when fossil fuels are combusted in a fluidized bed of a sulfur-acceptor additive and (2) the regeneration of this additive for reuse and the recovery of the sulfur.

Fossil fuels have been combusted in fluidized beds of either limestone or dolomite and in either an excess or a deficiency of oxygen. Combustion with an excess of oxygen is typical of utility and process steam plant operations. Oxygen-deficient combustion might have potential for producing a low-Btu gas that can be burned in gas turbines in a combined cycle plant.

When sulfur contained in coal is released during combustion in an oxygen-excess environment, $CaSO_4$ is formed; in an oxygen-deficient environment, CaS is formed. For regenerating $CaSO_4$, two favored regeneration methods are being studied. One is reductive decomposition of $CaSO_4$ to CaO (or to $CaCO_3$ in 10-atm operation) and SO_2 at $\sim$2000°F. A relatively concentrated stream of SO_2 is produced which can be processed in a sulfur recovery plant. The other method is a two-step process in which $CaSO_4$ is reduced to CaS at $\sim$1600°F and then the CaS is reacted with CO_2/H_2O at $\sim$1200°F to release H_2S for sulfur recovery.

Equipment

The bench-scale, atmospheric-pressure fluidized-bed combustion equipment consisted of a 6-in.-dia, 6-ft-long combustor with ancillary equipment including gas supplies, control valves and metering systems, a gas preheater, mechanical powder feeders for introducing coal and additive, and an off-gas particulate removal system consisting of two cyclones and a final filter.

During the year, the atmospheric unit was replaced with a combustion system designed for 10-atm operation, and testing of this equipment has started. The pressurized combustor is a 6-in.-dia unit with a pressurized shell surrounding the heated zone. Additionally, a 3-in.-dia pressurized regenerator has been constructed that will be operated separately from the combustor. The same gas-feed and same off-gas equipment will be used for the new combustor and the regenerator, though not simultaneously.

Equilibria of chemical reactions have been studied in a laboratory-scale static system, using a horizontal, 3-in.-dia reactor. The two-step regeneration reactions have been studied in a 2-in.-dia, batch fluidized-bed reactor equipped with the necessary gas supplies, particulate handling equipment, and analytical systems.

Bench-Scale Combustion Experiments at One Atmosphere Pressure

Combustion of coal in a deficiency of air has been studied to obtain data on sulfur species formed in the gas phase and bed, on NO levels in the flue gas, and carbon losses from the combustor. Oil combustion studies with excess air present have explored the effects of the main operating variables on sulfur retention in the bed and NO levels in the flue gas; combustion efficiencies for oil combustion and coal combustion experiments have been compared.

Coal Combustion Experiments with a Deficiency of Oxygen. Coal combustion experiments were made at fluidized-bed temperatures of 1450-1650°F and a range of air feed rates. When the air flow rate was decreased (starting from a slightly oxygen-excess condition), the following were observed:

1. The ratio, $H_2S/(H_2S+SO_2)$, increased in the effluent gas.

2. Sulfur retention apparently decreased initially. With further decreases in air feed rate and thus a more oxygen-deficient condition, H_2S formation increased and sulfur retention rapidly increased. It is postulated that since oxygen is required for form $CaSO_4$, decreasing the amount of oxygen fed decreased the chance for $CaSO_4$ to form. As a result, more of the SO_2 released during combustion left in the flue gas, lowering sulfur retention. As the quantity of oxygen fed decreased further, H_2S was mainly formed. H_2S reacts rapidly with additive.

3. The CO and hydrocarbon concentrations in the flue gas increased.

4. The sulfide content of the bed increased. Sulfite in low concentrations was also found in the bed.

5. The carbon content of the bed increased as did the quantity of carbon elutriated from the bed.

6. The NO level in the flue gas (<200 ppm) was lower than in the oxygen-excess experiments (>300 ppm). With an oxygen deficiency, less NO appeared to be formed at higher combustion temperatures and less at greater oxygen deficiencies.

A two-stage combustion concept appears to have good prospects for low sulfur emissions. In this concept, the first-stage fluidized bed is operated under conditions that favor H_2S formation (i.e., feeding of air at rates constituting large oxygen deficiencies). In the second stage, combustible gases from the first stage are burned with excess air. Prospects that NO emission would be decreased by the two-stage combustion concept seem good, but it has not yet been determined whether the gas leaving the first stage contains nitrogen compounds other than NO and whether such compounds would be oxidized to NO in the second stage.

Oil Combustion Experiments with an Excess of Oxygen. Residual fuel oil (containing 1.97 wt % S) was burned in an excess of oxygen. Operating conditions were bed temperatures of 1450 to 1650°F, Ca/S mole ratios up to 11.9, a gas velocity of ∿3 ft/sec (except for one experiment at 5.5 ft/sec), and 3 vol % oxygen in the flue gas (except in one experiment with 1 vol % oxygen in the flue gas).

The following observations were made on the basis of experimental results:

1. The effect of temperature on sulfur retention was similar to that observed in coal combustion experiments--i.e., there is a temperature yielding maximum sulfur retention. In the oil-combustion experiments, maximum sulfur retention was at 1500-1550°F.

2. The shape of the curve for sulfur retention as a function of Ca/S mole ratio resembles that obtained in coal combustion experiments. In the oil combustion runs, sulfur retention increased as Ca/S mole ratio was increased to about 5, then leveled off at 90% as the Ca/S ratio was increased further. The slope of the curve for sulfur retention as a function of Ca/S ratio in the oil combustion runs is less steep than the slope for the combustion of Illinois coal (3.7 wt % sulfur) at similar operating conditions.

3. When oil was combusted (in the experiments with 3% O in the flue gas), the NO levels in the flue gas ranged from 110 to 150 ppm. This may be compared with the 400-800 ppm range observed when coal was burned.

Cyclone Collection Efficiencies During Coal Combustion Experiments. Data on particle-removal efficiency of the ANL cyclone separators were obtained as a basis for estimating the dust loading and the needed filter area of a cartridge filter for the recently constructed pressurized combustion bench-scale plant. In the atmospheric-pressure system, flue gas passed through two cyclones in series, which have been modified for operation with the pressurized equipment, and a final filter.

Collection efficiencies (defined as ratio of the weight of particles removed to the weight of particles entering the cyclones) were compiled for 26 earlier ANL experiments in which the dust loadings at the combustor exit were 0.16 to 1.78 g/ft^3.* The combined efficiency of the two cyclones was above 80% in 24 of the 26 experiments and above 90% in 21 of the experiments. The dust loading in the flue gas leaving the second cyclone averaged 0.06 g/ft^3 for the 26 runs; the maximum loading was 0.22 g/ft^3.

Combustion Efficiencies for Coal and Oil Combustion with Excess Air. The combustion efficiency for experiments performed in the combustor was determined as the ratio of carbon burned to carbon fed, multiplied by 100. Carbon loss was calculated by determining unburnt carbon leaving the system by three routes: (1) carbon associated with the elutriated solids, (2) incompletely burned gases, i.e., carbon monoxide and hydrocarbons, and (3) carbon associated with fluidized-bed material taken from the system. In no experiment was there recycle of fines.

Combustion efficiencies were 93 to 96% in ten coal-combustion experiments with oxygen concentrations in the flue gas of about 3% and a fluidized-bed temperature of 1600°F. In all experiments, carbon losses in the bed material were negligible. Only about 10-20% of the carbon loss was due to the formation of carbon monoxide and hydrocarbons. The major carbon loss (80-90%) occurred as a result of elutriation of incompletely combusted fine particles in the exhaust gases.

Combustion efficiency in oil-combustion experiments (bed temperatures ranged from 1450-1650°F) was similar to that observed for coal combustion experiments, ranging from 94 to 96% for experiments with 3% O_2 in the flue gas. Combustion efficiencies were lower when there was less excess oxygen in the flue gas and when gas velocities were higher. In oil combustion, the major carbon loss occurred as a result of incomplete burning of the CO and hydrocarbons formed during combustion.

Regeneration of Sulfur-Containing Additives

When coal is burned in a fluidized bed containing limestone or dolomite additive, the product of the reaction between sulfur-containing gases and additive is calcium sulfate if combustion is carried out under oxidizing conditions or calcium sulfide if combustion is carried out with a deficiency of air.

Several regeneration processes are under consideration. These are

---

*All volume measurements, unless indicated otherwise, are at 70°F and one atmosphere absolute pressure.

1. Reductive decomposition of calcium sulfate to form $CaCO_3$ and SO_2 (under the proposed operating conditions).

2. Roasting of calcium sulfide in air or oxygen to form SO_2 and CaO (or $CaCO_3$).

3. Reaction of calcium sulfide with steam and carbon dioxide to form H_2S and $CaCO_3$.

Processes 2 and 3 can be used to regenerate not only calcium sulfide, but also material containing calcium sulfate if the sulfate is first reduced to the sulfide.

Another alternative is to thermally decompose the $CaSO_4$, but too high a temperature would be required for this process if a high-SO_2-content gas were to be obtained. For example, at 2500°F, the SO_2 equilibrium pressure is only 0.06 atm.

The thermodynamics of the above processes were considered, and the yields of gaseous sulfur-containing products, the compositions of solid phases, and the variations of these yields and compositions with temperature, pressure, and gas composition for a system at equilibrium were calculated.

Reductive Decomposition of $CaSO_4$. To test the accuracy of the equilibrium compositions calculated for the reduction of $CaSO_4$ with CO/CO_2 mixtures, experiments have been performed in a static system. The apparatus consists of a horizontal tube reactor fabricated from recrystallized alumina and equipped with the required gas supplies and sampling points. The tube is 36 in. long and has an ID of 3 in. with 1/4-in. walls. One end of the alumina reactor is closed, and the opposite end is capped with a stainless steel O-ring flange. Except for the flanged end, the tube is enclosed within a furnace for temperature control.

Experimental results show good agreement, in most cases, between experimental and calculated values of SO_2 levels when $CaSO_4$ was reacted with CO/CO_2 over a range of ratios. The data also indicate that CO and SO_2 were being slowly removed by a secondary process. Analyses of the gas samples indicate that reaction was occurring in the ratio of one mole of SO_2 to one mole of CO, forming one mole of CO_2 during the period of equilibration at 1900°F (the other reaction product was probably elemental sulfur, which was found at the cooler end of the alumina tube).

Two-Step Process. A second regeneration procedure of interest is to first reduce the $CaSO_4$ to CaS at 1600-1700°F and then to react the CaS at 1000-1300°F with CO_2-H_2O to form $CaCO_3$ and H_2S. Experimental data on these process steps were obtained in a 2-in.-dia batch fluidized-bed reactor.

Conversion of $CaSO_4$ to CaS. The effect of temperature on the rate of reduction of $CaSO_4$ to CaS with H_2 and CO was studied. Results showed that with partially sulfated dolomite and approximately three stoichiometric equivalents of hydrogen added over the 5-hr period, less of the bed material was converted to sulfide at 1350°F than at either 1450°F or 1600°F at equivalent times. Percent conversions after 4.5 hr at 1350°F, 1450°F, and

1600°F were 18%, 38%, and 86%, respectively. An additional experiment was performed with CO, and conversion using CO agreed with the expected conversion using H_2 at the temperature employed (1500°F).

Reaction of CaS with CO_2/H_2O. The product of each of the reduction experiments was carbonated (i.e., the unreacted CaO was reacted with CO_2 to form $CaCO_3$) at 10 atm to simulate a product that would be obtained in an actual 10-atm combustion-reduction experiment. This material was then reacted batchwise with an equimolar mixture of CO_2/H_2O at 900 to 1100°F, a gas velocity of approximately 1 ft/sec, and 10-atm pressure, and the H_2S concentration in the outlet gas was monitored.

The results showed that:

1. The reaction producing H_2S was initially rapid, but the rate decreased after a short time. Typically, the reaction rate dropped nearly to zero after several minutes.

2. The peak concentration of H_2S in the outlet gas was high, near the expected equilibrium value.

3. Typically, half or less of the CaS reacted.

In continuing work, the effects of process variables are being studied in an attempt to increase the quantity of CaS reacted.

Sulfation-Regeneration Cyclic Experiments. Since it will be desirable to reuse additive material a number of times in commercial applications, a cyclic experiment has been performed to obtain data on the pickup and removal of sulfur from additive particles and to measure decrepitation and attrition of additive particles during sulfation-regeneration cycles. Six cycles of simulated combustion and two-stage regeneration were performed with a single bed of additive. The starting material (1.2 kg) was part of the final bed from a coal combustion experiment in which dolomite No. 1337 had been used as additive. The initial sulfur content of this material was 15.4 wt %. The experiment was performed batchwise in the 2-in.-dia fluidized-bed reactor and a cycle consisted of sulfation (in all except the first cycle), reduction of the $CaSO_4$ to CaS with H_2 or CO reductant, and reaction with CO_2/H_2O gas mixture to convert the CaS to $CaCO_3$. A sample of the bed material was taken after each step in the cycle and analyzed for sulfur and sulfide content.

The data for the regeneration step showed that the peak concentration of H_2S in the effluent gas was 13 vol % (dry basis) in cycle 1 and decreased to 0.5 vol % (dry basis) for cycles 5 and 6. The percentage of the calcium sulfide converted to CaCO decreased to a very low indeterminant value after several cycles. It appears from these data that a layer of material of low permeability is built up on or within pores of the additive particles, inhibiting the removal of sulfur. The high sulfur loading of the bed particles in these experiments may be a factor in poor conversion.

Sulfiding-Regeneration Experiments. Because the presence of $CaSO_4$ might have contributed to the poor sulfur removals noted in the sulfation-regeneration experiment discussed above, several cyclic experiments were performed with dolomite or limestone starting beds in which the $CaCO_3$ constituent was reacted directly with H_2S, and then the product CaS was reacted with CO_2/H_2O. The $MgCO_3$ in the dolomite bed was calcined before the H_2S reaction. Preliminary experimental results showed that:

1. The regeneration reaction was initially rapid, but slowed after a short time.

2. The peak concentration of H_2S in the outlet gas during regeneration was near the expected equilibrium value in the first cycle.

3. The shapes of the curves for sulfur removal from the gas phase by limestone and dolomite during H_2S sorption tests appeared to be similar--sulfur was initially removed at a high rate with each type of sorbent, and not all sulfur was removed.

Pressurized Combustion and Regeneration Pilot Plant

Description. Equipment has been installed for combusting coal at pressures up to 10 atm and for regenerating sulfated lime for reuse. The equipment consists of a regenerator and fluidized-bed combustor which have a common off-gas system (cyclones, filters, gas-sampling equipment, pressure let-down valve, and scrubber). The two vessels will not be operated simultaneously.

The combustion unit consists of a 6-in. schedule 40 pipe (Type 316 stainless steel), approximately 11 ft long, with an outer shell consisting of 12-in. schedule 10 pipe (Type 304 stainless steel) over nearly the entire length. A bellows expansion joint is incorporated into the outer shell to accommodate differential thermal expansion of the inner and outer vessels.

The regenerator has a 3-in. ID. It consists of a 2 1/2-in. layer of Plibrico castable refractory encased in an 8-in. schedule 40 pipe (316 stainless steel). This entire assembly is enclosed in a pressure shell made of 12-in. schedule 20 carbon steel pipe.

Petrocarb Solids-Feeder Tests. The suitability of a modified-standard Model 16 ABC Petrocarb solids feeder for feeding coal or limestone to a pressurized combustor was tested. Uniform feed rates in the range of 20 to 100 lb/hr are required in the high-pressure combustion system.

Tests were made at atmospheric and at ∿80 psig pressure. Higher feed rates, in general, gave more uniform solids flow than did lower ones; sized, dried coal (1.2 wt % moisture, 20-200 mesh) flowed more evenly than as-received coal (4.0 wt % moisture, -14 mesh). A 5/16-in. orifice in the mixing valve was the smallest that could be used with -14 mesh coal without sporadic plugging. When the length of the transport line was increased, lower feed rates were achieved. However, results of these tests showed that the feeder was not suitable for feeding at the lower feed rates.

II. INTRODUCTION

Methods are being developed for lowering the concentrations of noxious pollutants emitted from power- and steam-producing plants to meet standards set by state and federal governmental agencies. Progress is reported here on a continuing study of the removal of pollutant (SO_2, NO, particulate) from the gas phase in the combustion of fossil fuels (such as coal, oil, and natural gas). The concept investigated involves introducing fuel and a sulfur-reacting additive material such as crushed limestone or dolomite into a hot fluidized bed of solids.

Two different combustion modes are possible, one with complete and the other with partial combustion of the fuel in the fluidized bed. In the complete-combustion mode (also called one-stage or oxygen-excess combustion), oxygen in excess of the stoichiometric amount required to burn the fuel to CO_2 and H_2O is fed to the fluidized bed. In the second mode (called two-stage or oxygen-deficient combustion), a deficiency of air is added to the fluidized bed, and the resulting H_2, CO and gaseous hydrocarbons are combusted to CO_2 and H_2O by providing additional oxygen (air) either in the region above the bed or in a separate combustor.

In the oxygen-excess combustion mode, the sulfur forms SO_2, which reacts with the calcium in limestone or dolomite to form $CaSO_4$

$$CaCO_3 + SO_2 + 1/2\ O_2 \rightarrow CaSO_4 + CO_2$$

In the oxygen-deficient combustion mode, the sulfur forms H_2S, which reacts to produce CaS

$$CaCO_3 + H_2S \rightarrow CaS + CO_2 + H_2O$$

Since relatively large quantities of limestone (compared to the quantity of coal ash) are required to efficiently remove the sulfur, regeneration of the sulfated or sulfided lime or dolomite will probably be desirable. Various regeneration schemes have been proposed, but the thrust of the program is toward selecting one of two processes. The first is one-step reductive decomposition of $CaSO_4$ at $\sim$2000°F.

$$CaSO_4 + CO \rightarrow CaCO_3 + SO_2$$

The second is a two-step scheme--reduction of $CaSO_4$ to CaS at 1600-1700°F, followed by reaction of the CaS with CO_2/H_2O at 1000 to 1300°F to release H_2S

$$CaSO_4 + 4\ CO \rightarrow CaS + 4\ CO_2$$

$$CaS + CO_2 + H_2O \rightarrow CaCO_3 + H_2S$$

Operation of the combustor system at 10-atm pressure is desirable in order to take advantage of advanced power cycle concepts. Here, pressurized gas from the combustor would operate a gas turbine to recover energy. Operation of the regeneration reactor at 10-atm pressure is desirable in order to match the pressure in the 10-atm combustor.

The Argonne National Laboratory (ANL) work on the control of pollutant emissions during fluidized-bed combustion of coal in excess oxygen at 1 atm pressure has been reported in previous annual reports in this series. The ANL work reported here has consisted of three major parts--(1) combustion studies, (2) regeneration studies, and (3) construction of a bench-scale, pressurized combustion and regeneration system. Coal was burned in one set of experiments in a deficiency of oxygen, and in another set of experiments oil was burned in an excess of oxygen (all experiments at atmospheric pressure). The oil combustion experiments complemented previous coal combustion tests made in excess oxygen. Regeneration studies have consisted of examination of the equilibria of different processes, experimental studies to determine equilibrium SO_2 levels in the reductive decomposition reaction, and experiments on the two-step process. Construction of the 10-atm regenerator and combustor pilot plants has been completed, and testing of the units has started.

III. BENCH-SCALE, ATMOSPHERIC COMBUSTION EXPERIMENTS

Objectives of the coal combustion and oil combustion experiments reported below were to determine the effects of different operating conditions on sulfur retention in the bed and NO levels in the flue gas, as well as combustion efficiencies. An additional objective of the coal combustion experiments was to determine the sulfur species formed in the gas phase and bed.

A. Materials

1. Coal

Two shipments of Illinois coal were used in coal combustion experiments, both from Peabody Coal Co. Mine 10, Seam 6, Christian County, Illinois (furnished by Commonwealth Edison).

Data on the chemical and physical characteristics of coal samples from the fourth shipment are presented in Table 1. The coal contained 4.1 wt % S (Table 1). Data on samples from the third shipment (see ANL/ES-CEN-1004[1]) showed that chemical characteristics were similar to the fourth shipment. The average particle diameter was smaller than in the fourth shipment, 350 μm and 429 μm.

2. Oil

The residual fuel oil used in the oil combustion experiments contained 1.97 wt % sulfur and had an SSF (Saybolt Seconds Furol) viscosity of 162.5 at 122°F and a flash point of 178°F. Other properties of this oil are listed in Table 2. It was obtained from Esso.[†]

3. Additives

Limestone No. 1359, used in the experiments reported here, was obtained from M. J. Grove Lime Co., Stephens City, Va. and contained ∿95 wt % $CaCO_3$ and ∿1 wt % $MgCO_3$. The average particle size was 609 μm.

4. Starting Bed Material

In most of the bench-scale experiments performed during the report period, the starting bed was calcined and partially sulfated limestone.

B. Equipment and Procedure

The major equipment item of the bench-scale combustor system (shown in Fig. 1 and described in detail in pp. 21-23 and Appendix B, ANL/ES-CEN-1004) is a vertical 6-in.-dia, 6-ft-high stainless steel combustor. To permit control of the combustor temperature during an experiment, three 230-V resistance heaters and four annular air-cooling chambers are mounted on the wall at the combustion zone (the lower 24 in. of the combustor).

[†]We are indebted to Mr. A. Skopp of Esso Research and Engineering Company for obtaining the oil for us.

TABLE 1. Some Chemical and Physical Characteristics of Coal from Fourth Shipment from Commonwealth Edison Co.

Source of Coal: Mine 10 (Peabody Coal Co.), Seam 6, Christian County, Illinois

Proximate Analysis,[a] wt %		Ultimate Analysis,[a] wt %	
Moisture	6.00	Carbon	62.94
Ash	12.70	Hydrogen	4.50
Volatile Matter	40.53	Nitrogen	1.25
Fixed Carbon	40.76	Chlorine	0.0
Heating value 11,304 Btu/lb		Sulfur	4.09
		Oxygen	8.48
		Ash	12.70

Sieve Analysis	
U.S. Sieve No.	wt %
-14 +25	22.9
-25 +35	11.1
-35 +45	11.0
-45 +80	15.8
-80 +170	15.5
-170 +325	9.5
-325	14.3

[a]Average of two samples.

TABLE 2. Properties of Esso Residual Fuel Oil Used in Combustion Experiments

API Gravity	14.6
Viscosity, SSF[a] at 122°F	162.5
Bottoms, Sediment and Water	0.5%
Flash Point	178°F
Pour Point	+15°F
Flow Point	+25°F
Sulfur	1.97%

[a]Saybolt Seconds Furol

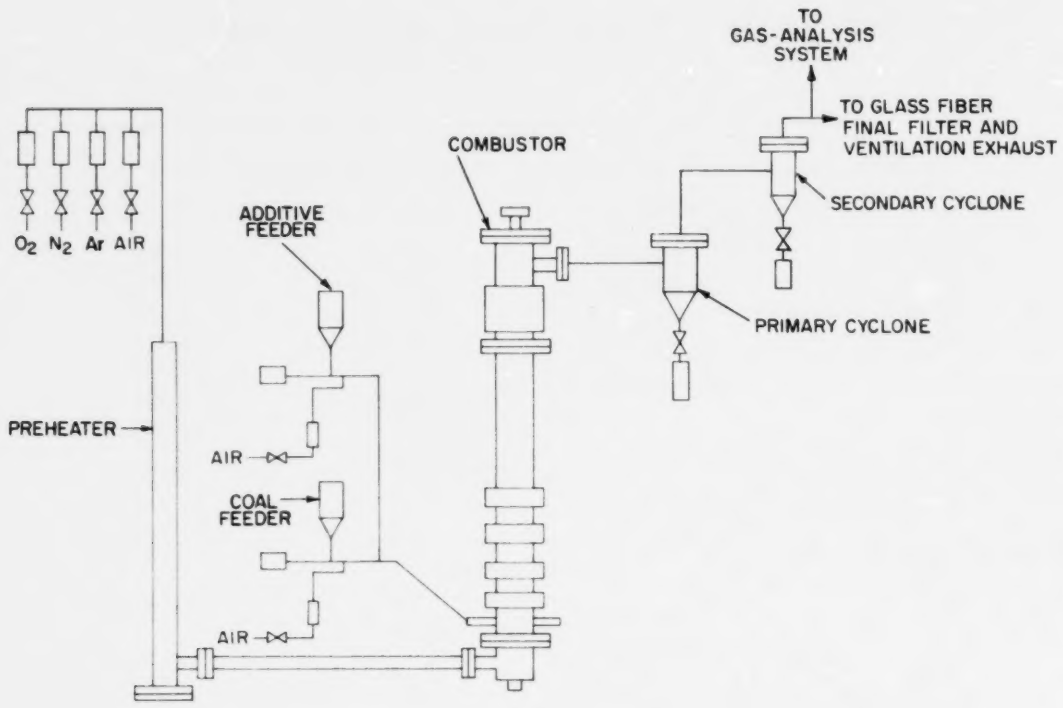

Fig. 1. Simplified Equipment Flowsheet of Atmospheric Bench-Scale Fluidized-Bed Combustor and Associated Equipment. ANL Neg. No. 308-2870.

Fluidizing air for the combustor that has been preheated in a 3-in.-dia, 7-ft-long electrically heated, packed pipe is fed into the combustor through a bubble cap gas distributor mounted on the bottom flange. Coal and additive are continuously fed into 3/8-in. stainless steel lines by variable-drive volumetric screw feeders mounted on scales. These solids are fed pneumatically (entrained in a transport air stream) into the fluidized bed at a point just above the gas distributor plate. Coal and fresh limestone are metered as they are fed. Flue gas leaving the combustor passes through a particle-removal system consisting of two in-series cyclones and a glass fiber final filter. Approximately one-twentieth of the flue gas that has passed through the second cyclone is diverted to the gas analysis system. The water content of this flue gas stream is reduced to 3000 ppm (by condensation and refrigeration) to prevent moisture interfering with gas analysis. Continuous analyses of the dried gas for NO, SO_2, CO, CH_4, and O_2 are carried out with infrared analyzers and a paramagnetic oxygen analyzer. Gas chromatography provides intermittent analyses for CO_2. All instrument signals, pneumatic and electrical, are routed to a data logger that produces a paper tape record for further data processing as well as a typed output of the signal values.

Solids leave the combustor (1) as bed samples, (2) as excess bed material, and (3) as elutriated flyash-limestone fines. Periodically during a run, the bed and the elutriated solids are sampled for chemical analysis (generally for C, Ca, S, and $CO_3^=$) and to obtain material balances. Bed material is removed intermittently (generally once per hour) during a run to maintain a constant bed height, the quantity removed depending on the quantities of limestone and coal fed and the quantities of solids elutriated as fly ash and removed as bed samples.

In startup of all oil and coal combustion runs, the fluidized bed of particulate solids is preheated to ∿1000°F by passing heated air through the bed and heating with the heaters mounted on the reactor wall. Coal, or oil, is introduced into the heated bed, ignites, and increases the bed temperature to the desired operating temperature (e.g., ∿1600°F). The bed is maintained within 10°F of the selected temperature by passing air or an air-H_2O mixture through annular chambers on the exterior of the combustor wall. Additive is introduced continuously into the bed. In the air-excess oil combustion experiments, the O_2 concentration in the flue gas was ∿3%

For coal combustion experiments made with a deficiency of combustion air, the coal feed rate is adjusted until the oxygen concentration in the flue gas is approximately 2%; the flow rate of air fed to the fluid bed is next reduced until the oxygen concentration in the flue gas reaches zero, then reduced an additional amount so that a deficiency of air is fed to the fluid bed. An oxygen concentration of zero in the flue gas was obtained at 1550°F with Peabody Mine 10 coal by lowering the air flow from an above-zero oxygen condition to about 80 ft^3 of air per pound of coal fed. Additional air for the two-stage experiments was injected above the bed region through a line that entered the top of the combustor.

For the oil combustion experiments, which were performed at atmospheric pressure, an oil feeding system (shown schematically in Fig. 2) was installed. The oil in the primary oil vessel was heated, and the tank was then pressurized to transfer the oil to the combustor. Near the combustor, air was injected into the transport line to impel oil into the bed. The in-line analytical instruments for measuring SO_2, NO, CH_4, CO, CO_2 and O_2 concentrations in the flue gas were the same as those used for the coal combustion runs.

C. Results and Discussion

1. Air-Deficient Coal Combustion Experiments

The concept of two-stage combustion provides for introduction into the fluidized bed (the first stage) of a substoichiometric quantity of air (that is, less air than is required to burn the coal completely to CO_2 and H_2O). Additional air may be injected into the disengaging section above the fluidized bed (the second stage) to burn gaseous hydrocarbons, H_2, and CO in the gas stream from the first stage.

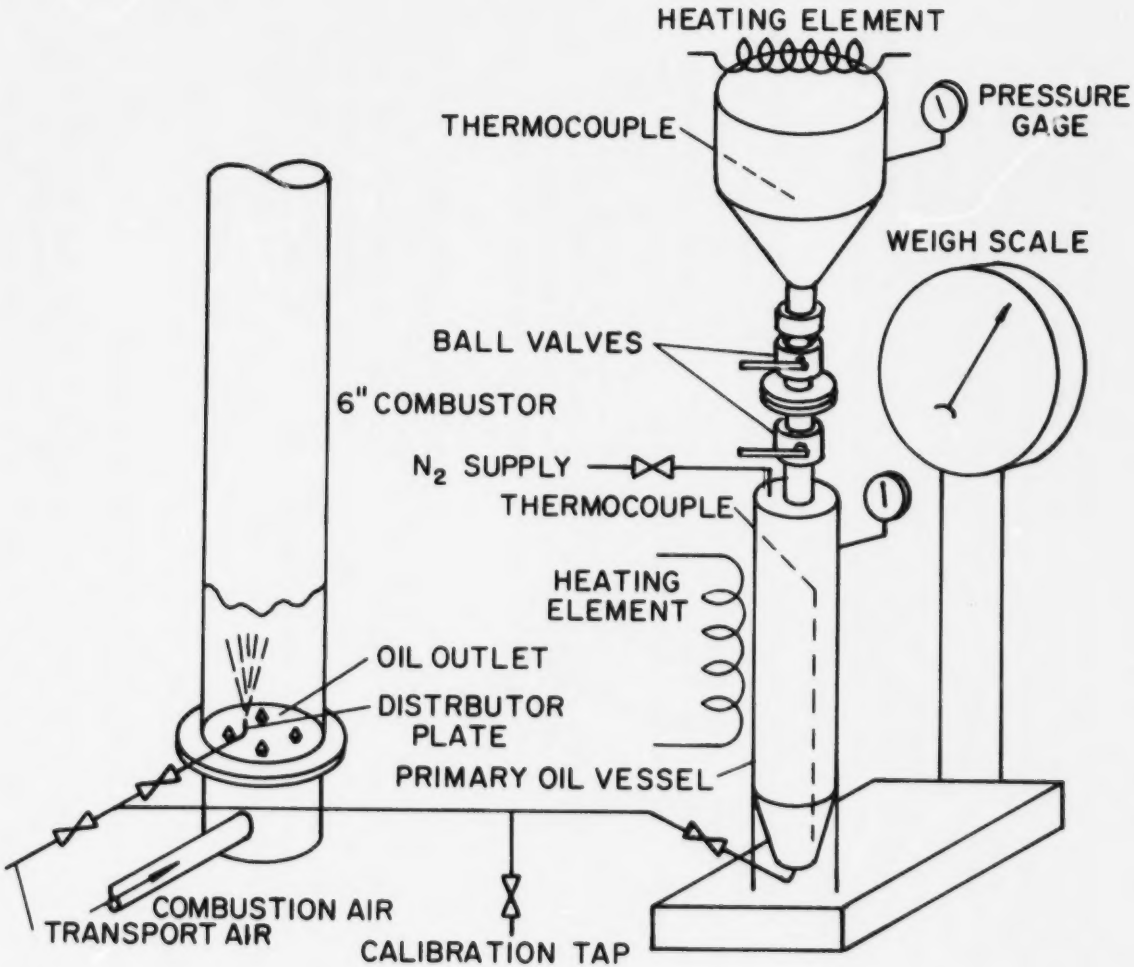

Fig. 2. Equipment for Feeding Oil to the 6-in.-dia Combustor

Two-stage combustion experiments of an exploratory nature were conducted to determine if this combustion mode might have benefits, as compared with single-stage fluidized-bed combustion. To simulate the condition of combustion in the first stage only, experiments were performed in which a substoichiometric quantity of air was introduced into the bottom of the fluidized bed but no secondary air was fed. In other experiments, secondary air was introduced above the fluidized bed. The bed consisted of coarse lime particles in most of these experiments. In a few experiments, coal was combusted in an Alundum bed to determine the $H_2S/(SO_2 + H_2S)$ ratios in the flue gas in the absence of limestone. In the lime bed experiments, limestone was fed continuously into the bed during the experiment; no limestone was fed during the alundum bed experiments.

a. Effect of Decreasing Air Input on Ratio of H_2S to (H_2S+SO_2) in Flue Gas. The concentration of H S in the off-gases was measured to determine which operating conditions affect the formation of this sulfur compound. In experiments in which air was introduced into the first stage only, the amounts of H_2S and SO_2 in the off-gas were compared. The percentage of sulfur in the off-gas as H_2S was sensitive to the amount of air introduced into the fluidized bed, increasing drastically when the air feed rate was reduced below a value corresponding to 70% of the stoichiometric quantity of air necessary to react with the coal fed* (see Fig. 3). At an air feed rate equivalent to 50% of the stoichiometric quantity, the concentration of H_2S (611 ppm) was nearly equivalent to the concentration of SO_2 (660 ppm). At air inputs of 70-80% of the stoichiometric quantity, the relative amount of sulfur as H_2S fell to about 2% of the total sulfur in the gas.

In those experiments in which secondary air was introduced above the fluidized bed (Fig. 3), the H_2S level in the off-gas was low--corresponding to less than 1% of the total sulfur in the gas. This suggests that any H_2S in the gas leaving the first stage is oxidized to SO_2 by air fed to the second stage.

No consistent relationship was apparent between H_2S level and either the temperature of the fluidized bed (1450-1650°F) or the temperature of the off-gas in the freeboard above the bed (1100-1800°F).

The ratio of H_2S to total sulfur (H_2S+SO_2) in the flue gas when coal was combusted in an alundum bed in the absence of limestone can be compared to the limestone experiments in Fig. 3. When oxygen could be detected in the flue gas, the relative H_2S concentration in the flue gas was low, less than 10% of the total sulfur in the flue gas. When oxygen is no longer detected in the flue gas, the concentration of H_2S increased rapidly.

Not all of the sulfur was released to the flue gas, i.e., H_2S+SO_2 levels in the flue gas were less than expected based on the coal

*Although the parameter, air feed rate as a percent of stoichiometric, was based on feed rates of coal and air, it is recognized that the quantity of coal actually oxidized varies with other parameters (i.e., temperature, etc.). For certain correlations, it may well be more suitable to use the parameter, stoichiometric air feed rate based on the coal actually oxidized.

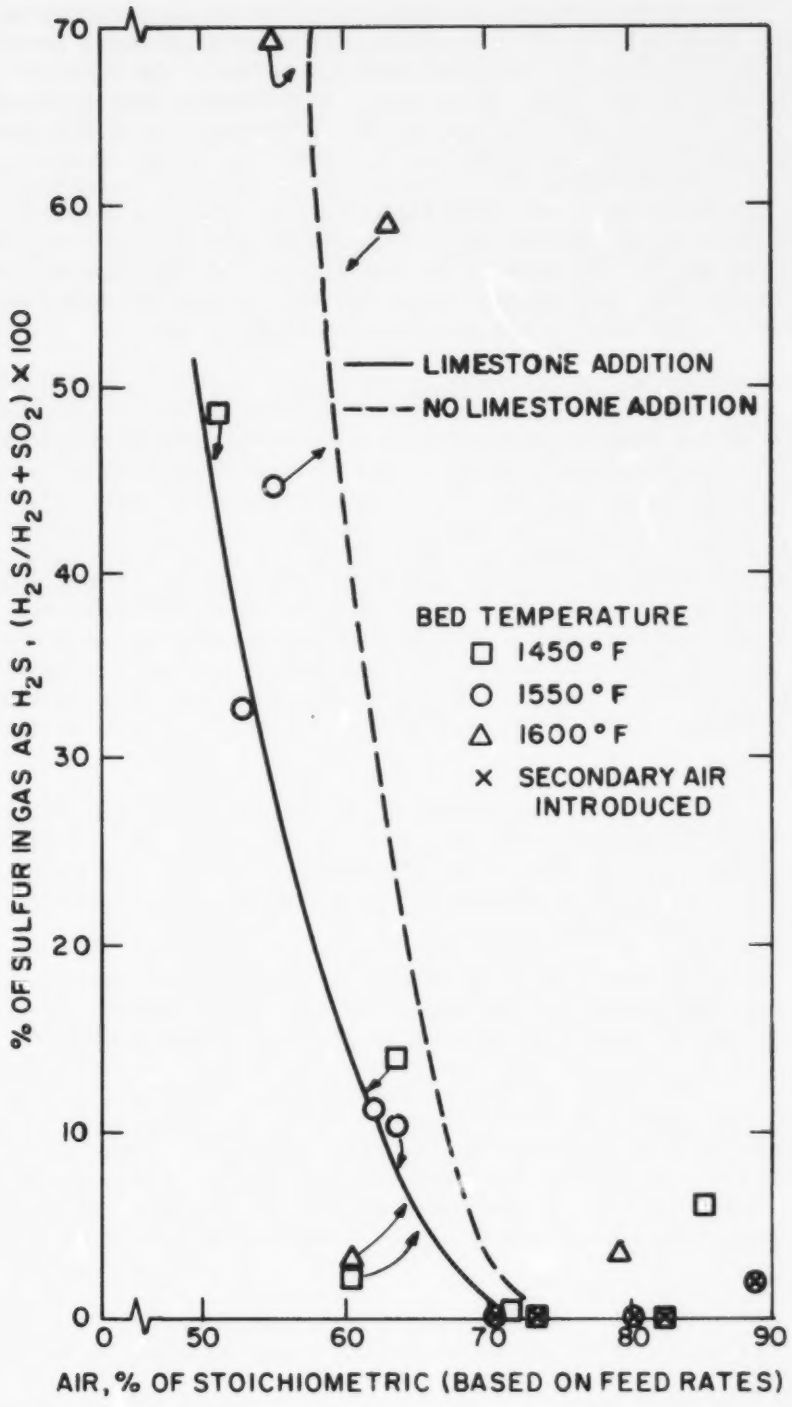

Fig. 3. Effect of Air Feed Rate on Percent of Sulfur in Off-Gas as H_2S

fed. Approximately 15% of the sulfur in the coal fed to the combustor was retained in the alumina bed. The bed at the end of the experiments contained ∿5.5 wt % sulfur (1.9% from the coal present in the bed at the end of the experiment and ∿3.6% from pickup of sulfur). At low stoichiometric air rates, the sum of the H_2S and SO_2 contents of the fuel gas was substantially less than the equivalent to the sulfur fed in the coal (less than 50%). This suggests that a large part of the sulfur might have been converted to sulfur vapor by a reaction between H_2S and SO_2 (Claus reaction) at some point in the system upstream from the analyzers.

b. Sulfur Retention. Sulfur retention is defined as the percentage of the sulfur associated with the coal feed that is not contained in the off-gas as SO_2 or H_2S.* Experiments were performed with no introduction of secondary air to determine sulfur retention as a function of the Ca/S mole ratio in the feed at 1450, 1550, and 1650°F (Fig. 4). Also shown in Fig. 4 (to allow comparison) is a curve representing data for experiments carried out earlier under single-stage oxygen-excess conditions at 1450-1470°F.

The data presented for the substoichiometric air experiments show a large amount of scatter--principally due to variation in the quantity of air fed to the fluidized bed, which was not the same in all experiments. The percent of stoichiometric air added in these experiments ranged from 51 to 91. The best sulfur retention was observed at air additions less than 60% of stoichiometric.

For experiments carried out at a Ca/S ratio of about 2 and temperatures of 1450-1650°F (Fig. 5), no simple relationship between the amount of air introduced into the bed and sulfur retention was evident; however, a line has been fitted to the points as shown. At an air feed rate of 100% of stoichiometric, sulfur retention was about 65%. As the air feed rate was decreased, sulfur retention first decreased to about 45% as the air rate decreased to 75% of the calculated stoichiometric requirement and then increased rapidly as the air rate was decreased further. This suggests that in an oxygen-deficient region (75-95% of calculated stoichiometry), removal of sulfur by lime in the form of SO_2 is poor, but that at lower air flow rates sulfur is in the form of H_2S and is efficiently removed. This would be expected because oxidizing conditions are required for the retention of SO_2 by lime (to convert a $CaSO_3$ intermediate to $CaSO_4$), whereas reducing conditions are required for the retention of H_2S by lime.

The introduction of secondary air above the bed resulted in erratic but generally lower sulfur retentions. The increased sulfur content of the off-gas after secondary air was introduced was probably caused by burning of entrained coal particles in the second stage to produce additional SO_2.

c. NO Levels in the Flue Gas. When coal was burned with a deficiency of air fed to the first stage, concentrations of NO in the off-gas from the first stage as a function of the amount of air introduced into the bottom of the fluidized bed were as shown in Fig. 6. To obtain these data

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*Because a small fraction of the carbon was not burned in these experiments and some sulfur is retained with the coal, the sulfur retention values given are probably higher than would be realized if all of the carbon were burned.

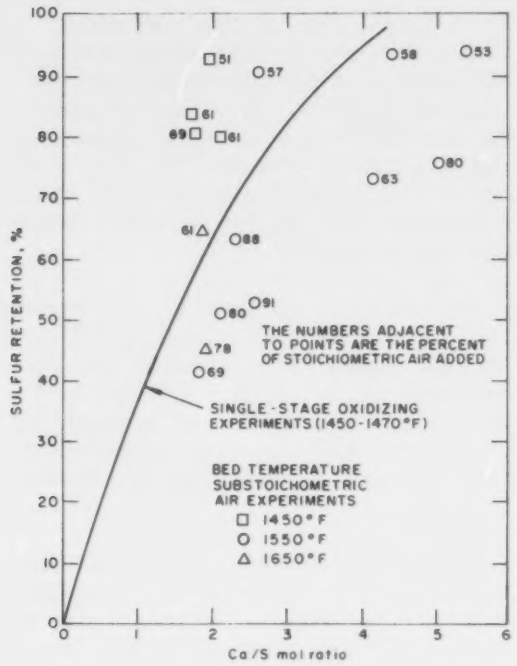
SULFUR RETENTION, %
Ca/S mol ratio
THE NUMBERS ADJACENT TO POINTS ARE THE PERCENT OF STOICHIOMETRIC AIR ADDED
SINGLE-STAGE OXIDIZING EXPERIMENTS (1450-1470°F)
BED TEMPERATURE SUBSTOICHOMETRIC AIR EXPERIMENTS
□ 1450°F
○ 1550°F
△ 1650°F

Fig. 4. Sulfur Retention in Oxygen-Excess and Oxygen-Deficient Experiments

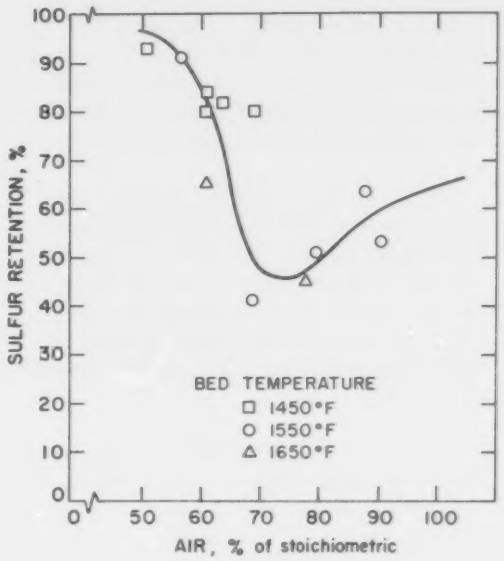

Fig. 5. Effect on Sulfur Retention of Air Feed Rate to First Stage
Ca/S mole ratio = 2
ANL Neg. No. 308-2875

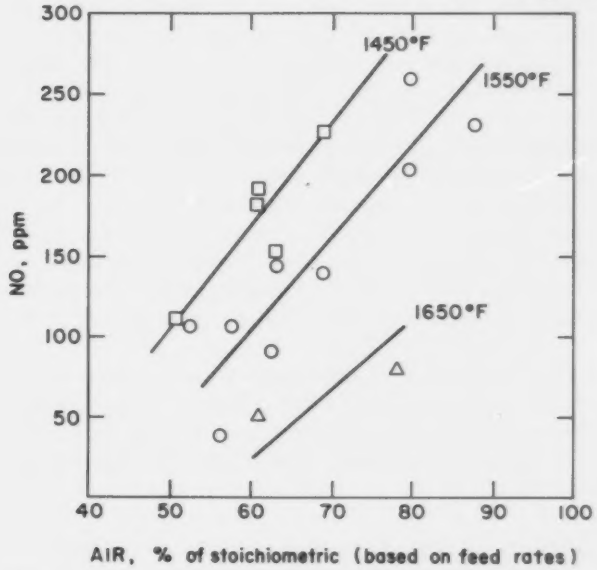

Fig. 6. Effect of Air Feed Rate and Fluidized-Bed Temperature on NO Concentration in Off-Gas from the First Stage during Combustion of Coal.
ANL Neg. No. 308-2871.

only the first stage was operated. The NO concentrations ranged from 50 to 250 ppm and apparently were affected by both the amount of air introduced and the temperature of the fluidized bed. At the lower air feed rates, the NO levels were generally lower. At a given air feed rate, NO levels were higher at lower bed temperatures. Since earlier work at ANL showed that nitrogenous compounds in coal are oxidized to NO during fluidized-bed combustion, it can be postulated that the lower levels of NO observed at higher temperature are due to more rapid decomposition of NO. This decomposition may be promoted by the presence of CO; another possibility is that nitrogenous compounds other than NO may be formed in the highly reducing atmosphere of the bed. The NO levels observed when coal was combusted with an excess of air were greater than 250 ppm.

The data presented in Fig. 6 are not corrected to an equivalent off-gas volume basis. However, if this correction were made, the dependence of NO emission on air feed rate would be even more pronounced, assuming that feed rates of coal were equivalent.

Upon the introduction of secondary air above the fluidized bed, NO levels in the off-gas varied erratically--usually increasing. Possible explanations for this behavior are (1) any reduction of NO by CO in the zone above the bed would be suppressed by introducing secondary air or (2) if a nitrogen compound such as ammonia was present in the gas, it might be oxidized to NO by the secondary air.

d. Sulfur Species in the Bed. Results show that the sulfide content of bed material decreased as air flow was increased. At air inputs corresponding to 50% of stoichiometric, as much as 100% of the sulfur in the bed was sulfide. In most experiments in which the air input exceeded 65% of stoichiometric, sulfide content dropped rapidly to less than 1%. No relationship was found between sulfide content and bed temperature.

The sulfite content of bed samples was erratic, ranging between 6.2 and <0.1 wt %. No correlation of sulfite content with either bed temperature or air feed rate could be found.

e. Carbon Balance. Carbon balances were made for three experiments; for three other experiments, all data for making the balances except the CO_2 level in the flue gas are available (see Table 3). The small quantity of carbon not accounted for is represented (1) by hydrocarbons (other than CH_4) for which no analyses were made and (2) by a small loss of fine carbon particulate from the combustion system. The data show that as the volume of air added to the bed decreases (experiments 14-1A, -1B, -2) at the same temperature, the CO content of the flue gas increases markedly, the CH_4 content increases slightly, and the quantity of carbon elutriated to the first and second cyclone separators from the fluidized bed increases.

The carbon content of the bed under low stoichiometric air additions (55%) was as high as 31% (expt. 14-3B). Under these conditions the amount of carbon elutriated was about 15% of that fed.

TABLE 3. Carbon Balances and Carbon Contents of Solids in Coal Combustion Experiments with a Deficiency of Air

EXPERIMENT	14-1A	14-1B	14-2	14-1C	14-3A	14-3B
Carbon in coal, g/hr	1428	1428	1684	1799	1485	1713
Carbon Out, g/hr						
First Cyclone	71	136	174	167	235	233
Second Cyclone	22	11	24	7	7	16
Flue Gas						
CH_4	>24	32	39	42	28	32
CO	42	350	441	521	330	455
CO_2	1230	N.D.*	840	N.D.	N.D.	800
Total Carbon Out, g/hr	>1470	N.D.	1632	N.D.	N.D.	1682
Carbon Concentration in Solids Streams, wt %						
Bed at End of Experiment	<1	<1	6	<1†	20	31
First Cyclone	29	39	46	39	47	62
Second Cyclone	52	53	55	56	35	53
Run Conditions						
Temp, °F	1450	1450	1450	1550	1600	1600
Coal Feed, lb/hr	5.0	5.0	6.3	5.9	5.2	6.0
Air, % of Stoichiometric	90	86	71	54	64	55

*N.D. - No Data

†Value appears to be low. Sufficient sample was not available for making another analysis.

f. Preliminary Evaluation of the Concept. Although the work conducted on two-stage combustion was exploratory in nature, a preliminary evaluation of the concept can be made. The principal advantages of the two-stage combustion concept over one-stage combustion are: (1) lower NO emissions, (2) retention of sulfur in the form of calcium sulfide (rather than sulfate) allowing for potentially easier regeneration of the additive, (3) production of a combustible gas that could be used in conjunction with a gas turbine.

The principal disadvantages are: (1) greater elutriation of carbon, (2) possible complications in additive regeneration owing to the high carbon content of the bed, (3) necessity for removing heat from the bed under conditions that might be corrosive to immersed steam tubes.

Sulfur retention appears to be roughly equal for the two concepts. It is notable, also, that no problems of coal caking were encountered even at high bed carbon contents. Further work might be warranted at lower air addition rates and higher bed temperatures to avoid the need for heat removal from the bed.

2. Oil Combustion Experiments with an Excess of Oxygen

To assess the removal of SO_2 from combustion gases when residual fuel oil is burned in a fluidized bed of sulfated lime with continuous feeding of limestone additive, experiments were performed in the 6-in.-dia fluidized-bed combustor at a variety of operating conditions. Residual fuel oil (containing 1.9% S) was burned in an excess of oxygen at bed temperatures ranging from 1450 to 1650°F, Ca/S mole ratios up to 11.9, a gas velocity of ~3 ft/sec (except for one experiment at 5.5 ft/sec), and with 3 vol % oxygen in the flue gas (except in one experiment with 1 vol % oxygen in the flue gas).

Table 4 lists operating data, concentrations of some components of the flue gas, and calculated sulfur retention and combustion efficiency data for the experiments in which limestone was fed to the combustor.

Effect of Temperature on SO_2 Retention. The effect of temperature on SO_2 retention is similar to that observed in coal combustion experiments (ANL/ES/CEN-1004, p. 25[1]), for which there is a temperature at which sulfur retention is at a maximum. In the oil-combustion experiments, maximum SO_2 retention was observed in the 1450-1650°F temperature range, possibly at a temperature below 1550°F (Fig. 7).

Effect of Ca/S Mole Ratio on Sulfur Retention. As in the coal combustion experiments, increasing the limestone feed rate at a fixed oil feed rate increased the sulfur retention (Fig. 8). The slope of the curve for sulfur retention as a function of Ca/S ratio is not as steep as in experiments made with Illinois coal containing 3.7 wt % sulfur. Also, the maximum observed sulfur retention of 90% is slightly lower than in the coal experiments at equivalent operating conditions.

Table 4

Operating Data and Results, Combustion of Residual Fuel Oil in Excess Air

Equipment: ANL 6-in.-dia fluidized-bed combustor

Oil: Esso residual fuel oil, 1.97 wt % sulfur

Additive: Limestone No. 1359, as received (94.8 wt % $CaCO_3$, 0.9 wt % $MgCO_3$ 609 μm average particle size)

Starting Fluidized Bed: 17.3 lb partially sulfated and calcined limestone No. 1359 (∿24-in. fluidized-bed depth) Note: The final bed from a run was used as the starting bed for the following run.

O_2 Concentration in Flue Gas: ∿3% (except 4A-1, 1%)

Expt. OIL-	Fluidized-Bed Temp (°F)	Oil Feed Rate (lb/hr)	Limestone Feed Rate (lb/hr)	Ca/S Mole Ratio	Gas Velocity (ft/sec)	Flue Gas Composition					Sulfur Retention (%)	Combustion Efficiency (%)
						SO_2 (ppm)	NO (ppm)	CO (ppm)	CH_4 (ppm)	CO_2 (%)		
2	1650	5.8	0.6	1.6	5.5	1350	135	8500	>3400	No Data	16	<92
3A	1550	3.3	0.8	4.1	3.2	630	110	6000	1500	14.4	60	95
3B	1550	3.0	2.2	11.9	3.2	170	140	6000	800	15.0	90	94
3C	1550	3.3	1.1	5.4	3.0	200	150	5000	1200	14.2	88	No Data
4A	1450	3.2	1.2	6.0	3.1	350	140	5000	1100	15.0	78	95
4B	1650	3.2	1.2	6.0	3.1	550	130	5000	1000	14.0	66	96
4A-1	1450	4.8	1.2	4.0	3.3	520	190	>12000	>3400	No Data	68	No Data

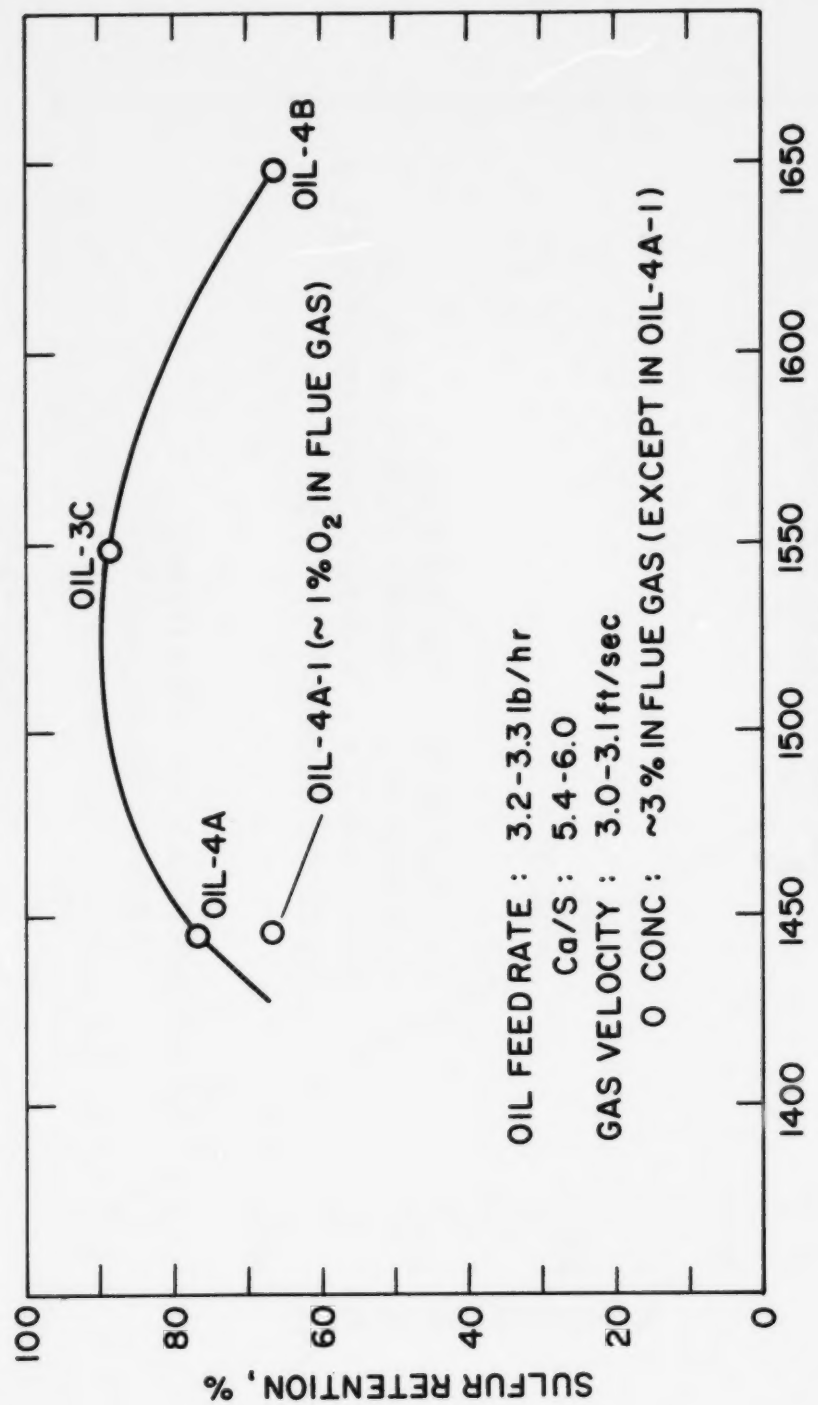

Fig. 7. Effect of Temperature on Sulfur Retention During Combustion of Residual Fuel Oil in Excess Air

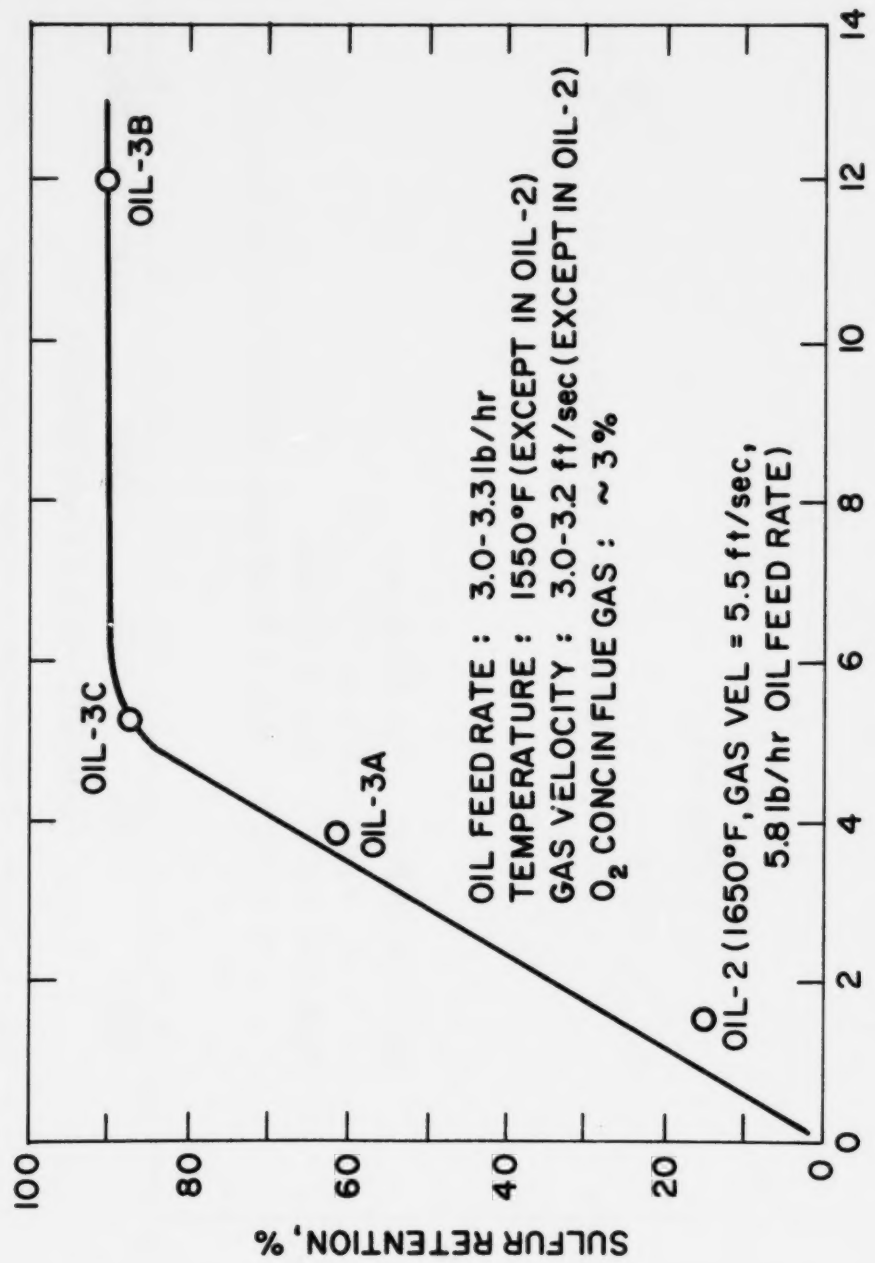

Fig. 8. Effect of Ca/S Mole Ratio on Sulfur Retention During Combustion of Residual Fuel Oil in Excess Air

NO Levels. Measured NO levels in the flue gas ranged from 110 to 150 ppm for experiments with 3 vol % oxygen in the flue gas. No trend was apparent related to an effect of fluidized-bed temperature or gas velocity on NO level.

Combustion Efficiency. Combustion efficiency, in percent, is defined as 100 (1 - carbon out/carbon in). "Carbon out" is the sum of carbon contents of elutriated solids, solids drained from the bed, and CO and hydrocarbons in the flue gas. "Carbon in" is the carbon content of the oil feed.

Combustion efficiency for the runs with 3 ft/sec gas velocity ranged from 94 to 96% (Table 4). In the single experiment made at a higher gas velocity of 5.5 ft/sec, the combustion efficiency dropped below 92%. An exact value could not be calculated because the CH_4 concentration (known to be above 3400 ppm) was not measured exactly. In the experiment with a 5.5 ft/sec gas velocity, considerable gaseous combustion was apparently taking place above the bed. The flame front was about two feet above the bed. The CH_4 and CO levels in the flue gas were high. Additionally, voluminous quantities of carbon floc were collected on the final filter. For these reasons, in subsequent experiments the oil feed rate and combustion air flowrate were lowered and the gas velocity was 3 ft/sec.

Bed temperatures in the 1450-1650°F range had little effect on combustion efficiency in the experiments.

The maximum carbon content of the fluidized-bed solids in the oil-combustion experiments was 1.1%. Most bed samples contained <1.0% carbon, the lower limit of detectability by the LECO combustion method. For the experiments with 3% excess oxygen and a gas velocity of 3 ft/sec, the carbon content of solids removed from the first cyclone ranged from 3.4 to 5.1% (a carbon loss of 3.7 to 8.5 g/hr from this source). For solids from the second cyclone, the carbon contents ranged from 6 to 20% (a loss of 0.2 to 0.8 g/hr of carbon from this source).

Particle Size Distribution and Bulk Density of Solids. Particle size distributions and bulk density data for the limestone additive, fluid bed, and solids from the primary and secondary cyclones are presented in Table 5 for experiment OIL-3C. For other runs, the bulk densities of the first and second cyclone solids ranged from 0.57 to 1.20 g/cc and from 0.23 to 0.68 g/cc, respectively.

Hydrogen Concentration in Flue Gas. The hydrogen concentration in the flue gas it not routinely measured with our available instruments. To obtain an estimate, five flue gas samples from the OIL-series experiments were analyzed with a gas chromatograph. The chromatographic column consisted of 3 ft of 1/4-in.-dia Molecular Sieve. Hydrogen concentration in the argon carrier gas was measured, using a thermal conductivity detector. The hydrogen concentrations in four samples from experiments made with 3% O_2 in the flue gas ranged from 46 to 340 ppm; for the experiment with 1% O_2 in the flue gas (OIL-4A-1), the hydrogen concentration was 2200 ppm.

TABLE 5. Particle Size Distributions and Bulk Densities for Solids Samples from Experiment OIL-3C

U.S.S. Screen Size	Percent in Screen Size Fraction, Bulk Density			
	Limestone Additive	Bed	Primary Cyclone	Secondary Cyclone
+40	42.0	81.1	3.1	1.3
-40+60	21.0	18.9	31.3	1.4
-60+100	12.9	--	24.1	1.7
-100+170	16.6	--	15.4	4.1
-170+270	6.7	--	8.4	75.2
-270	0.8	--	17.7	16.3
Bulk Density, g/cc	1.7	2.4	1.1	0.4

3. Cyclone Collection Efficiencies During Coal Combustion Experiments

Data on the particle removal efficiency of the cyclone separators were obtained as a basis for estimating the dust loading and filter area of a cartridge filter for the recently constructed pressurized combustion bench-scale plant. In the atmospheric-pressure system, flue gas passed through two cyclones in series, which have been modified for operation with the pressurized equipment, and a final filter. (The diameter of the first in-line cyclone is 6 5/8 in. and the diameter of the second is 4 1/2 in.)

To determine the adequacy of the glass fiber mat filters used in the atmospheric plant, collection efficiencies (defined as ratio of the weight of particles removed to the weight of particles entering the cyclone) were compiled for 26 earlier ANL experiments. The flue-gas flowrates ranged from 8 to 14 cfm, the coal feed rates from 4 to 7.3 lb/hr, and the additive feed rates from 1.1 to 2.3 lb/hr; the dust loadings at the combustor exit were 0.16 to 1.78 g/ft^3. The combined efficiency of the two cyclones was above 80% in 24 of the 26 experiments and above 90% in 21 of the experiments. The dust loading in the flue gas leaving the second cyclone averaged 0.06 g/ft^3 for the 26 runs; the maximum loading was 0.22 g/ft^3.

4. Combustion Efficiencies for Coal, Oil, and Natural Gas Combustion with Excess Air

The combustion efficiency for excess air experiments performed in the combustor was determined as the ratio of carbon burned to carbon fed, multiplied by 100. The carbon loss was calculated by determining unburnt carbon leaving the system by three routes: (1) carbon associated with the elutriated solids, (2) incompletely burned gases, i.e., carbon monoxide and hydrocarbons, and (3) carbon associated with fluidized-bed material taken from the system. All experiments were conducted without recycle of fines. Oxygen concentration in the flue gas in these experiments was approximately 3%.

Combustion efficiencies in ten coal-combustion experiments (made at a fluidized-bed temperature of ~1600°F) ranged from 93 to 96%.[2] In all experiments, carbon losses in the bed material were negligible. Only about 10-20% of the carbon loss was due to the formation of carbon monoxide and hydrocarbons. The major carbon loss (80-90%) occurred as a result of elutriation of incompletely combusted fine particles in the exhaust gases. Combustion efficiency can be increased by recycling the elutriated ash-carbon mixture to the fluidized bed or to a carbon burnup cell.

Combustion efficiency in oil combustion experiments (fluidized bed temperatures of 1450-1650°F) was similar to that observed for coal combustion experiments under similar conditions, ranging from 94 to 96% for experiments with 3% O_2 in the flue gas. Combustion efficiencies were lower when there was less excess oxygen in the flue gas and when gas velocities were higher. In oil combustion, the major carbon loss occurred as a result of incomplete burning of the CO and hydrocarbons formed during combustion. Combustion efficiency can probably be improved by operating the combustor with a deeper bed or by increasing the freeboard temperature.

In the combustion of natural gas, the elutriation of carbon-bearing fine particles is negligible and the major loss of unburnt carbon is in the carbon monoxide and hydrocarbons in the flue gas. Combustion efficiencies, calculated from analyses of samples of the flue gas, ranged from 94.1 to 99.2% at 1600°F in runs with 3% oxygen in the flue gas.[2] At 1800°F, combustion efficiencies were 94.1-98.8%. These results are similar to data reported by the USSR on combustion of gas in a fluidized bed.[3] Although the USSR data indicate that combustion efficiency is principally affected by bed temperature, combustion efficiency is also likely to be a function of bed depth, gas velocity, and excess oxygen concentration. For example, in an experiment at 1800°F, combustion efficiency was decreased to 91% when combustion conditions were intentionally made more reducing, i.e., 1.5 vol % O_2 in the flue gas rather than 1.8-4.5 vol % O_2.

IV. REGENERATION OF SULFUR-CONTAINING ADDITIVES

When coal is burned in a fluidized bed containing limestone or dolomite additive, the product of the reaction between sulfur-containing gases and additive is calcium sulfate if combustion is carried out under oxidizing conditions or calcium sulfide if combustion is carried out with a deficiency of air. As the capacity of the bed material to retain sulfur is approached, bed material must be removed from the combustor and replaced with fresh material. Simply discarding the sulfur-bearing material would be unattractive because of (1) the cost of replacement material, (2) the cost of transporting fresh material to the furnace and used materials from the furnace, (3) disposal costs, and (4) pollution problems associated with the disposal of used material (especially if it contained calcium sulfide, which would slowly release hydrogen sulfide if exposed to air). A process for regenerating used bed material so that the lime may be recycled through the combustor is needed, both to circumvent these problems and to recover the sulfur value as sulfuric acid or elemental sulfur.

Several regeneration processes have been considered. These are

1. thermal decomposition of calcium sulfate to form SO_2 and CaO,
2. reductive decomposition of calcium sulfate to form CaO and SO_2,
3. roasting of calcium sulfide in air or oxygen to form SO_2 and CaO,
4. reaction of calcium sulfide with water and carbon dioxide to form $CaCO_3$ and H_2S.

SO_2 or H_2S would be converted to sulfur in a Claus plant or to H_2SO_4 in an acid plant. Processes 3 and 4 can be used to regenerate not only calcium sulfide, but also material containing calcium sulfate if the sulfate is first reduced to the sulfide. Information is needed so that the most economical and effective process may be identified.

A. Thermodynamic Analysis of Some Schemes for Regenerating Partially Spent Additive from the Fluidized-Bed Combustion of Coal

Valuable information can be gained by considering the thermodynamics of the regeneration processes. The yields of gaseous sulfur-containing products, the compositions of solid phases, and the variations of these yields and compositions with temperature, pressure, and gas composition for a system at equilibrium can all be calculated. Optimum reactant feed ratios and gas compositions necessary to reduce a given feed of spent additive can also be calculated easily when product concentrations, compositions, and pressures are specified.

The equilibrium predicted product yield is, in effect, the upper limit (i.e., the maximum amount of gaseous sulfur species) for a reaction system operated in accord with the stated equilibrium system. Although equilibrium considerations are of utility in indicating the limits of the system, they cannot foretell the mechanism or kinetics of the reaction system, which can be elucidated only by experiment. Because a large variety of reactions can occur, a mixture of products at equilibrium is quite probable.

The following predictions and conclusions are based on the assumption that chemical equilibrium is achieved among the various phases. This implies that the rates of all relevant chemical reactions are large for the time scales being used, which scales are determined by mass transport rates within the system. The maximum rates of all reactions at which this supposition is valid vary with temperature and must be determined in the laboratory and in the pilot plant. It is further assumed that the system is not stoichiometrically limited. There must always be at least small amounts of the appropriate solid phases present for the results of these calculations to be valid. In actual processes, it is not expected that all of these solid phases will be present, however.

The assumption is also made that solid solutions do not form to any great extent. Exploratory experiments to date support this assumption. For the calculation of equilibrium data, values of the free energy of formation of the relevant compounds for the temperature range 1000-2500°F were compiled (Table 6). They are standard free energies of reaction (all gases at one atmosphere); the actual free energies of reaction will depend on the conditions existing in the regenerator during reduction.

The SO_2 pressures predicted from the free energies agree with the pressures measured in exploratory experiments (see Section B below), indicating that no serious inaccuracies exist in the free energy data.

1. Thermal Decomposition of Calcium Sulfate

Calcium sulfate decomposes by the reaction in Eq. 1 to give sulfur trioxide.

$$CaSO_4 \rightleftarrows CaO + SO_3 \qquad K_p = P_{SO_3}\ (atm) \tag{1}$$

The sulfur trioxide decomposes by the reaction in Eq. 2 to give sulfur dioxide and oxygen.

$$SO_3 \rightleftarrows SO_2 + 1/2\ O_2 \qquad K_p = \frac{P_{SO_2}(P_{O_2})^{1/2}}{P_{SO_3}} \tag{2}$$

The pressure of sulfur dioxide calculated from Eq. 2 is exactly equivalent to that calculated from Eq. 3.

$$CaSO_4 \rightleftarrows CaO + SO_2 + 1/2\ O_2 \qquad K_p = P_{SO_2} P_{O_2}^{1/2} \tag{3}$$

Equation 3 represents the decomposition of calcium sulfate to sulfur dioxide and oxygen. As can be seen from Table 7, the pressures of both sulfur dioxide and sulfur trioxide at any temperature likely to be of interest are too small to make thermal decomposition attractive. In this calculation of SO_2 pressure, it was assumed that no oxygen was present other than that from the decomposition of $CaSO_4$. The presence of additional oxygen would, of course, decrease the SO_2 pressure.

TABLE 6. ΔG°_f, Free Energy of Formation (kcal/g-mole)

RT(kcal) °K °F	1.6113 810.94°K 1000°F	1.7217 866.49°K 1100°F	1.8321 922.05°K 1200°F	1.9425 977.60°K 1300°F	2.0528 1033.16°K 1400°F	2.1633 1088.72°K 1500°F	2.2737 1144.27°K 1600°F	2.3841 1199.83°K 1700°F
CO[a]	-43.843	-45.096	-46.240	-47.385	-48.556	-49.725	-50.886	-52.045
CO_2[a]	-94.560	-94.583	-94.603	-94.621	-94.638	-94.655	-94.668	-94.681
CH_4[a]	-0.253	1.270	2.601	4.043	5.494	6.951	8.416	9.883
COS[a]	-50.415	-50.528	-50.668	-50.802	-50.939	-51.073	-51.211	-51.345
H_2O[a]	-48.504	-47.786	-47.063	-46.334	-45.600	-44.862	-44.118	-43.373
H_2S[a]	-11.972	-11.329	-10.685	-10.036	-9.386	-8.735	-8.081	-7.425
SO_2[a]	-72.382	-71.409	-70.436	-69.463	-68.492	-67.523	-66.554	-65.585
SO_3[a]	-77.756	-75.581	-73.410	-71.250	-69.099	-66.954	-64.821	-62.692
$CaCO_3$[b]	-237.340	-234.055	-230.776	-227.488	-224.216	-220.954	-217.662	-214.368
CaO[c]	-130.637	-129.304	-127.960	-126.599	-125.238	-123.876	-122.471	-121.054
CaS[b]	-109.249	-107.971	-106.682	-105.377	-104.038	-102.676	-101.315	-99.954
$CaSO_3$[c]	-224.478	-219.680	-214.739	-209.936	-205.139	-200.335	-196.314	-191.449
$CaSO_4$[3b]	-268.204	-262.300	-256.414	-250.538	-244.707	-238.895	-233.098	-227.297
NO[a]	19.159	18.891	18.823	18.655	18.359	18.319	18.151	17.983
NO_2[a]	19.994	20.837	21.689	22.532	23.382	24.225	25.072	25.914
MgO[a]	-122.788	-121.374	-119.919	-118.401	-116.879	-115.338	-113.797	-112.257
MgS[a]	-78.862	-77.512	-76.121	-74.669	-73.197	-71.712	-70.224	-68.735
$MgSO_4$[a]	-227.334	-221.320	-215.281	-209.206	-203.139	-197.078	-191.048	-185.024

(contd.)

TABLE 6. ΔG°_f, Free Energy of Formation (kcal/g-mole) (contd.)

RT (kcal) °K °F	2.4944 1255.38°K 1800°F	2.6049 1310.96°K 1900°F	2.7152 1366.5°K 2000°F	2.8257 1422.1°K 2100°F	2.9360 1477.6°K 2200°F	3.0463 1533.2°K 2300°F	3.1568 1588.8°K 2400°F	3.2673 1644.3°K 2500°F
CO[a]	-53.199	-54.353	-55.498	-56.642	-57.781	-58.919	-60.055	-61.184
CO_2[a]	-94.692	-94.703	-94.711	-94.719	-94.725	-94.732	-94.738	-94.742
CH_4[a]	11.353	12.828	14.304	15.784	17.262	18.742	20.222	21.702
COS[a]	-51.478	-51.613	-51.745	-51.878	-52.012	-52.146	-52.280	-52.411
H_2O[a]	-42.624	-41.873	-41.118	-40.361	-39.603	-38.842	-38.080	-37.319
H_2S[a]	-6.771	-6.114	-5.439	-4.803	-4.148	-3.492	-2.836	-2.181
SO_2[a]	-64.617	-63.649	-62.684	-61.719	-60.757	-59.793	-58.829	-57.869
SO_3[a]	-60.577	-58.463	-56.366	-54.272	-52.192	-50.116	-48.044	-45.989
$CaCO_3$[b]	-211.058	-207.759	-204.475	-201.237	-197.999	-194.761	-191.523	-188.285
CaO[c3]	-119.610	-118.161	-116.721	-115.286	-113.871	-112.437	-110.991	-109.570
CaS[b]	-98.510	-97.071	-95.688	-94.264	-92.840	-91.416	-89.992	-88.570
$CaSO_3$[c]	-186.584	-181.718	-176.857	-171.987	-167.140	-162.271	-157.392	-152.543
$CaSO_4$[3b]	-221.538	-215.795	-210.116	-204.466	-199.024	-193.478	-187.932	-182.388
NO[a]	17.813	17.645	17.477	17.306	17.138	16.968	16.800	16.631
NO_2[a]	26.761	27.605	28.447	28.951	30.128	30.968	31.811	32.647
MgO[a]	-110.716	-109.121	-107.321	-105.136	-102.375	-99.617	-96.864	-94.125
MgS[a]	-67.243	-65.698	-63.948	-61.813	-59.102	-56.393	-53.690	-51.001
$MgSO_4$[a]	-179.042	-173.008	-166.805	-160.228	-153.115	-146.019	-138.944	-131.922

[a] JANAF Thermochemical Data, issued by Dow Chemical Company, Midland, Mich.

[b] Fundamental Study of Sulfur Fixation by Lime and Magnesia, Final Report, Contract PH 86-66-108, Battelle Memorial Institute (June 30, 1966).

[c] J. P. Coughlin, Contributions to the Data on Theoretical Metallurgy, U.S. Bureau of Mines Bulletin NO. 542 (1954).

TABLE 7. Pressure of SO_3 and SO_2 in Equilibrium with $CaSO_4$ (assuming no O_2 pressure other than that from decomposition)

Temp (°F)	P_{SO_3} (atm)	P_{SO_2} (atm)
1700	1.16×10^{-8}	1.45×10^{-5}
1900	2.95×10^{-7}	1.78×10^{-4}
2100	4.31×10^{-6}	1.93×10^{-3}
2300	3.90×10^{-5}	1.20×10^{-2}
2500	2.72×10^{-4}	5.97×10^{-2}

2. Reductive Decomposition of Calcium Sulfate

a. Reductive Decomposition of $CaSO_4$ with CO/CO_2 Mixtures. The relative amounts of the species in an equilibrium mixture from the reduction of calcium sulfate with carbon monoxide-carbon dioxide mixtures can be calculated after the solid phases present at the various conditions of temperature and carbon monoxide/carbon dioxide ratio have been determined. The possible sulfur-containing solids are considered to be calcium sulfate, calcium sulfite, and calcium sulfide.

(1) Conditions for the Presence of $CaSO_4$ and CaS

The solid phases present at equilibrium with a P_{CO}/P_{CO_2} of 0.005-0.055 and temperatures of 1600 to 2400°F are shown in Fig. 9 (in which temperature is the ordinate and P_{CO}/P_{CO_2} the abscissa). Examination of the expression for K_p in the following reaction

$$1/4\ CaSO_4 + CO \rightleftarrows 1/4\ CaS + CO_2 \qquad K_p = \frac{P_{CO_2}}{P_{CO}} \tag{4}$$

shows that for any temperature, there is but one ratio of carbon monoxide to carbon dioxide at which calcium sulfate and calcium sulfide can coexist at equilibrium. The coexistence conditions appear as the line running from the lower left to the upper right of Fig. 9 and represent the CO/CO_2 ratios at which CaS and $CaSO_4$ can both be present at equilibrium. In the area to the right of this line, the gas mixture is so rich in carbon monoxide that calcium sulfate is completely reduced to calcium sulfide. To the left of the line, the gas mixture is so rich in carbon dioxide that calcium sulfide is completely oxidized to calcium sulfate. This line is called the coexistence line for calcium sulfate and calcium sulfide.

(2) Conditions for the Presence of Calcium Sulfite

Calcium sulfite is not stable in the presence of CO/CO_2 mixtures at any temperature from 1500 to 2400°F. This has been established by plotting "coexistence" lines for calcium sulfite with calcium sulfate and for calcium sulfite with calcium sulfide (Fig. 10). These are analogous to the calcium sulfate-calcium sulfide coexistence line described above and are determined in the same way from the equilibrium constants for reactions 5 and 6.

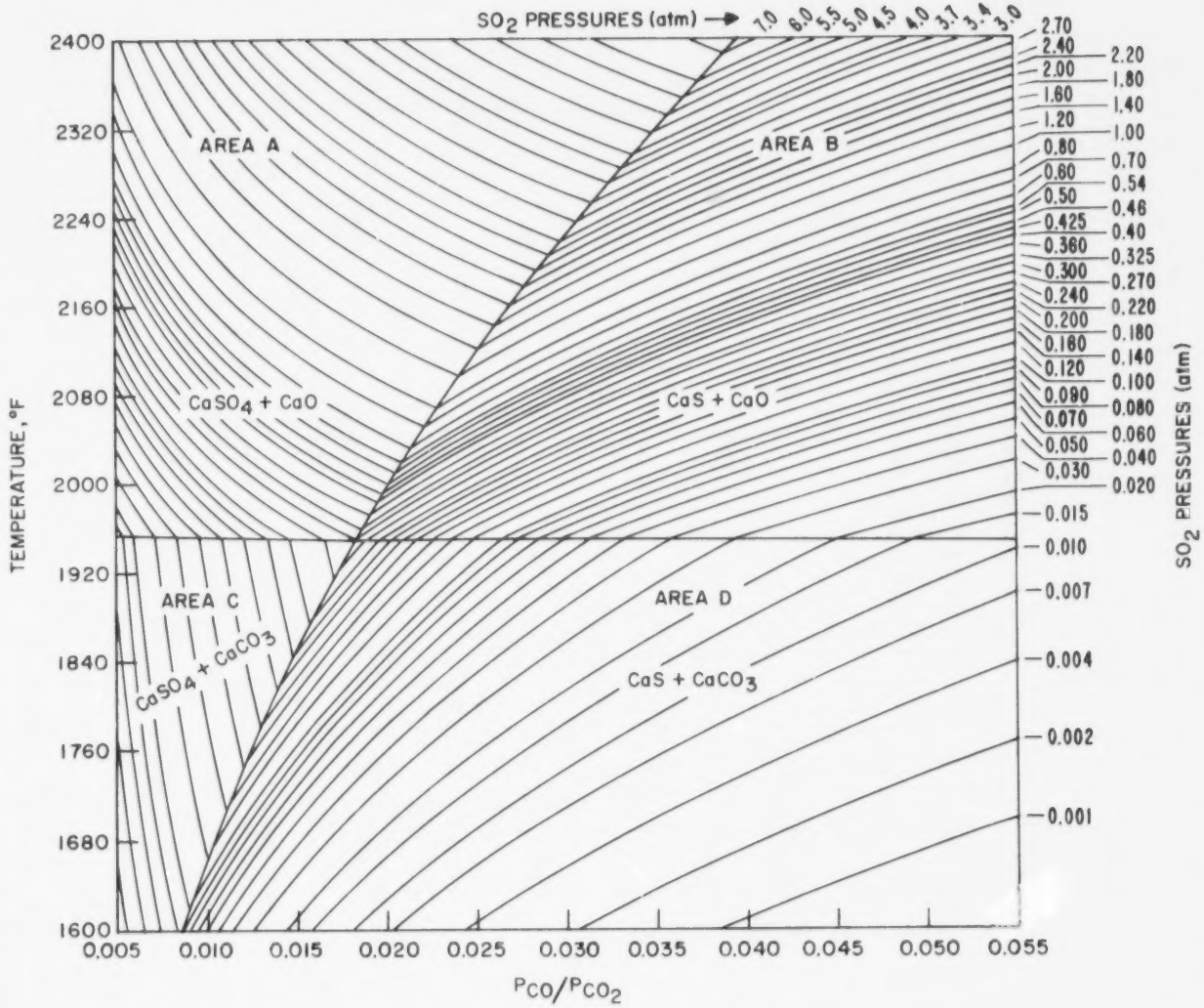

Fig. 9. Pressure of SO_2 in Equilibrium with CO/CO_2 Mixtures as a Function of Temperature (10-atm total pressure)

$$CaSO_4 + CO \rightleftarrows CaSO_3 + CO_2 \qquad K_p = \frac{P_{CO_2}}{P_{CO}} \tag{5}$$

$$1/3\ CaS + CO_2 \rightleftarrows 1/3\ CaSO_3 + CO \qquad K_p = \frac{P_{CO}}{P_{CO_2}} \tag{6}$$

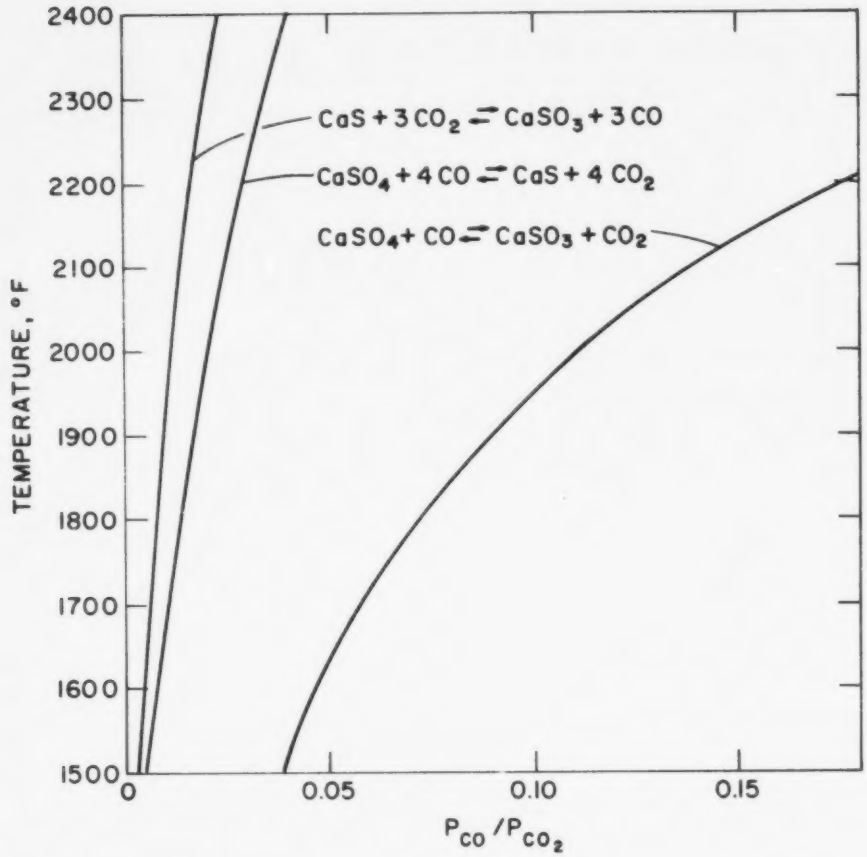

Fig. 10. Temperature and CO/CO_2 Conditions for Formation of $CaSO_4$, $CaSO_3$, and CaS

(3) Conditions for the Presence of $CaCO_3$ and CaO

When calcium sulfate is reduced or calcium sulfide is oxidized by a mixture of CO and CO_2, calcium oxide is formed. However, in the presence of carbon dioxide at sufficient pressure, calcium oxide is converted to calcium carbonate (Fig. 11).

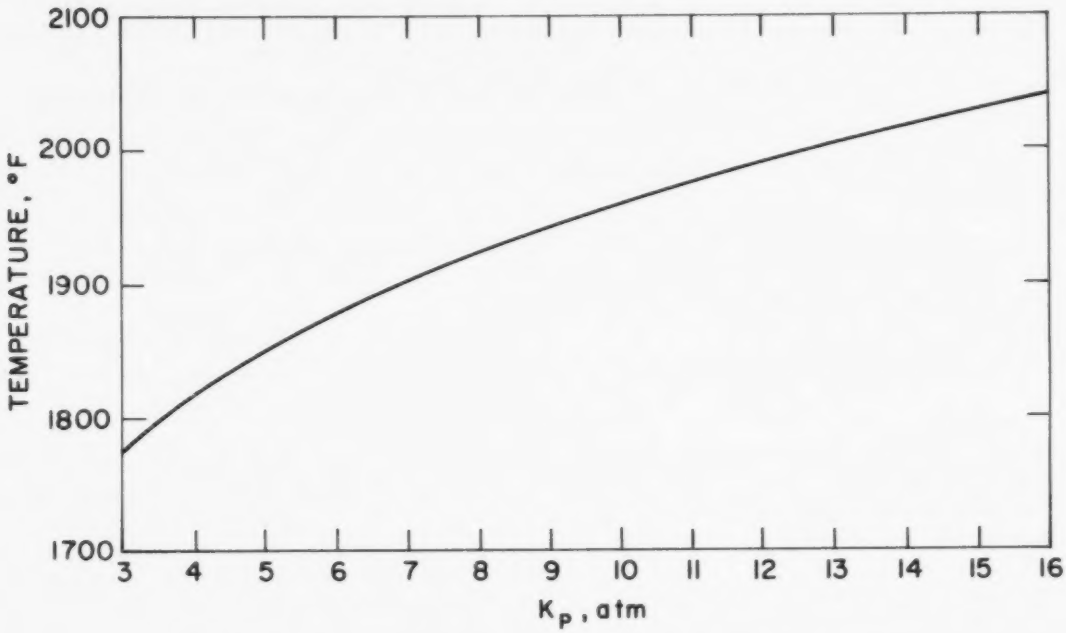

Fig. 11. Equilibrium Dissociation Pressure of $CaCO_3$ as a Function of Temperature

($CaCO_3 \rightleftharpoons CaO + CO_2$)

A coexistence line for the carbonate and the oxide is determined by the equilibrium dissociation pressure of calcium carbonate (reaction 7)

$$CaCO_3 \rightleftharpoons CaO + CO_2 \qquad K_p = P_{CO_2} \tag{7}$$

It also appears as a nearly horizontal line at about 1950°F in Fig. 9. This line represents the temperature at which the partial pressure of CO_2 in the equilibrium mixture just equals the equilibrium pressure of CO_2 over calcium carbonate.

The partial pressure of CO_2 in the equilibrium mixture is obtained by assuming a total pressure of 10 atm and subtracting the pressures of SO_2 and CO. Clearly, if the total pressure is lowered or if an inert gas

is added, the pressure of CO_2 will be lower and the horizontal line will be at a lower temperature. It is also clear that calcium carbonate does not exist above the horizontal line and that calcium oxide does not exist below it.

(4) Sulfur Dioxide Pressure

The pressure of sulfur dioxide in the equilibrium mixture can be calculated from the CO/CO_2 ratio and the equilibrium constant of the reaction appropriate to the part of Fig. 9 under consideration; however, in the areas labeled C and D, one must generate independent information about the CO_2 pressure by making assumptions exactly analogous to those made in the above discussion of calcium carbonate.

In area A of Fig. 9, SO_2 is generated by the following reaction:

$$CaSO_4 + CO \rightleftarrows CaO + SO_2 + CO_2 \qquad K_p = \frac{P_{SO_2} P_{CO_2}}{P_{CO}} \tag{8}$$

The pressure of SO_2 is shown as a family of isobars slanted down toward the right. In area B, SO_2 is generated by the oxidation of calcium sulfide in accordance with the following reaction:

$$1/3\ CaS + CO_2 \rightleftarrows 1/3\ CaO + CO + 1/3\ SO_2 \qquad K_p = \frac{\left(P_{SO_2}\right)^{1/3} P_{CO}}{P_{CO_2}} \tag{9}$$

The isobars of constant SO_2 pressure in area B curve down to the left, meeting those of area A at the calcium sulfide-calcium sulfate coexistence line. At any temperature, the SO_2 pressure is at a maximum at this junction. For example, at 2000°F, the maximum attainable equilibrium pressure of SO_2 is 0.46 atm at a CO/CO_2 ratio of 0.020. This maximum in the SO_2 pressure may be understood by examination of the appropriate equilibrium constants. For example, the expression for the equilibrium constant for reaction 8 predicts that the pressure of SO_2 is directly proportional to the CO/CO_2 ratio. Thus, the pressure of SO_2 must increase as the CO/CO_2 ratio increases as long as reaction 8 obtains. From the expression for the equilibrium constant in reaction 9, it may be seen that the SO_2 pressure is inversely proportional to the cube of the CO/CO_2 ratio. Thus, the SO_2 pressure increases with decreasing CO/CO_2 ratio as long as reaction 9 obtains. Reactions 8 and 9 occur simultaneously only along the coexistence line. Thus, as one moves away from the coexistence line, the SO_2 pressure must decrease.

In area C, reaction 10 applies.

$$CaSO_4 + CO \rightleftarrows CaCO_3 + SO_2 \qquad K_p = \frac{P_{SO_2}}{P_{CO}} \tag{10}$$

In this area, the pressure of SO_2 is dependent only on K_p and carbon monoxide pressure, and the SO_2 isobars are nearly vertical. The main effect results from the variation of K_p with the temperature. In area D, the SO_2 pressure is once again a strong function of the CO/CO_2 ratio as may be seen from reaction 11.

$$CaS + 4\ CO_2 \rightleftarrows CaCO_3 + SO_2 + 3\ CO \qquad K_p = \frac{P_{SO_2}\left(P_{CO}\right)^3}{\left(P_{CO_2}\right)^4} \qquad (11)$$

The slope of the isobars in area D differs only slightly from the slope in area B as a result of increased dependence on CO_2 pressure in area D.

(5) Sulfur Pressure

The pressure of sulfur vapor is quite low ($<10^{-2}$ atm) over the temperature range 1700 to 2300°F (Fig. 12). The pressure of sulfur in area B from reaction 12 was calculated.

$$CaS + CO_2 \rightleftarrows 1/2\ S_2 + CO + CaO \qquad K_p = \left(P_{S_2}\right)^{1/2} \frac{P_{CO}}{P_{CO_2}} \qquad (12)$$

Since the formation of sulfur is entirely analogous to the formation of SO_2, sulfur concentration may be expected to exhibit the same sort of maximum at the calcium sulfide-calcium sulfate coexistence line.

(6) Carbonyl Sulfide Pressure

The carbonyl sulfide pressure from reaction 13 was calculated.

$$CaS + CO_2 \rightleftarrows CaO + COS \qquad K_p = \frac{P_{COS}}{P_{CO_2}} \qquad (13)$$

Since P_{COS} is dependent on the pressure of CO_2, assumptions made in calculating COS pressure are similar to those made in the discussion of calcium carbonate. P_{COS} is low ($\sim 10^{-3}$ atm) in this system.

(7) Solid-Solid Reaction of CaS with $CaSO_4$

SO_2 is generated by the reaction of calcium sulfide with calcium sulfate, as is shown in reaction 14.

$$1/3\ CaS + CaSO_4 \rightleftarrows 4/3\ SO_2 + 4/3\ CaO \qquad K_p = \left(P_{SO_2}\right)^{4/3} \qquad (14)$$

Since reaction 14 is exactly equivalent to the sum of reactions 8 and 9, the SO_2 pressure calculated from reaction 14 must be just that calculated from reaction 8 or reaction 9, using the CO/CO_2 ratio at the coexistence line. Another way of saying this is that the presence of both calcium sulfide and calcium sulfate determines an oxidizing potential for the atmosphere with which it is in equilibrium, and this oxidizing potential determines the CO/CO_2 ratio of the atmosphere. If carbon monoxide and carbon dioxide are present in the gas phase over a mixture of calcium sulfide and calcium sulfate, they serve as a facile route to the production of SO_2 so that rapid reaction rates for mixtures of the two solids are possible.

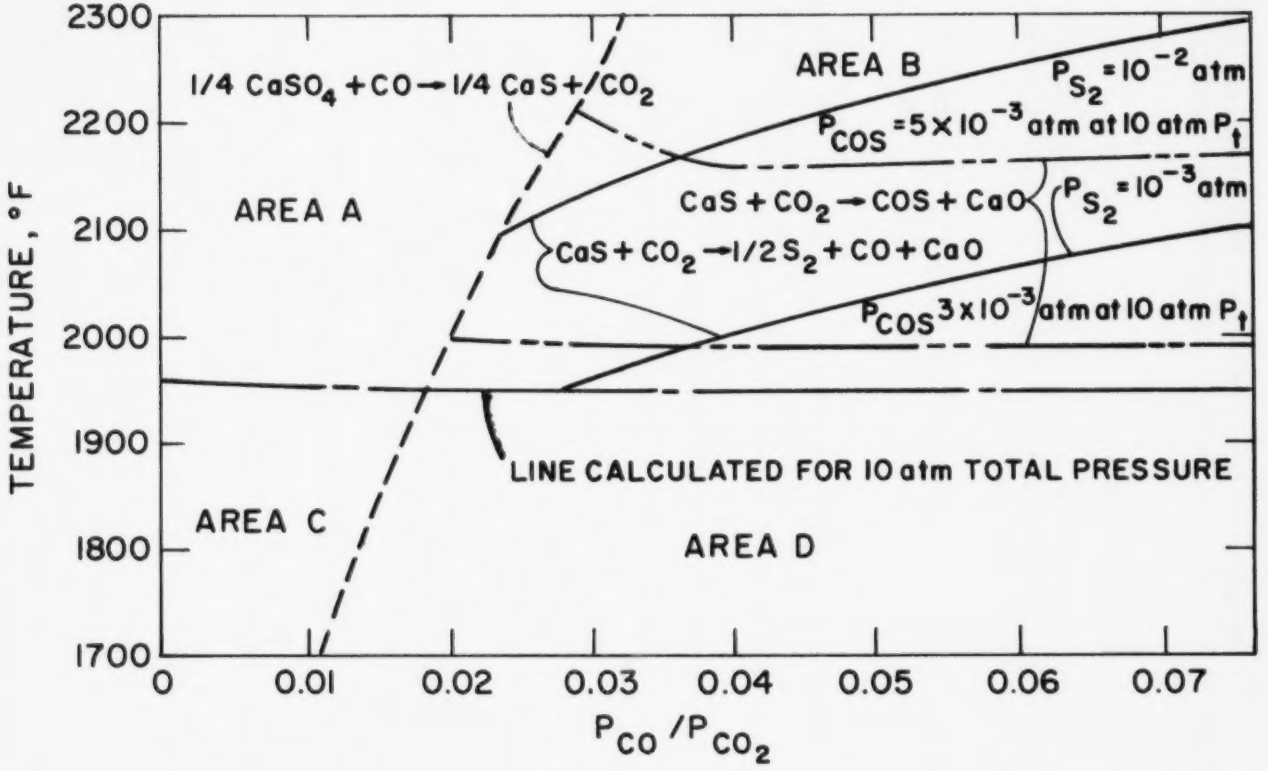

Fig. 12. S_2 and COS Concentrations at Equilibrium as a Function of Temperature and CO/CO_2 Ratio

b. Reduction of $CaSO_4$ with H_2/H_2O Mixtures. The system calcium sulfate-calcium sulfide-H_2-H_2O is exactly analogous to the system calcium sulfate-calcium sulfide-CO-CO_2. This means that all the features of the CO-CO_2 system are present in the H_2-H_2O system. The sulfur-containing solid phases once again are calcium sulfate and calcium sulfide, but calcium oxide and calcium hydroxide are the non-sulfur-containing solid phases. The pressure of SO_2 at a given temperature has a maximum value where the calcium sulfate and calcium sulfide are in equilibrium with the H_2-H_2O mixture (Fig. 13). The instability of calcium sulfite can be shown in the same way as in the CO-CO_2 system. In fact, the major differences between the H_2-H_2O system and the CO-CO_2 system are that carbonyl sulfide is replaced with H_2S (see Fig. 12 for the pressure of H_2S and sulfur vapor as a function of temperature and H_2/H_2O ratio) and that at any given temperature, the numerical value for the H_2/H_2O ratio differs from that of the CO/CO_2 ratio.

An additional difference between the systems is that in the H_2-H_2O system, calcium hydroxide can form at lower temperatures and higher pressures of H_2O (just as $CaCO_3$ can form in the CO-CO_2 system). However, at 10-atm H_2O pressure, $Ca(OH)_2$ is not stable above 1200°F.

For any temperature and SO_2 pressure, the H_2/H_2O ratio can be calculated from the equivalent CO/CO_2 ratio via reaction 15.

$$H_2 + CO_2 \rightleftarrows H_2O + CO \qquad K_p = \frac{P_{CO}/P_{CO_2}}{P_{H_2}/P_{H_2O}} \tag{15}$$

This is the familiar water-gas shift reaction. The principle involved here is that equal SO_2 pressures are obtained in the H_2-H_2O system and the CO-CO_2 system when the oxidizing potentials of the atmospheres are the same, i.e., when the two atmospheres would be in equilibrium with each other.

An important conclusion is that the maximum pressure of SO_2 from any system in which calcium sulfate is reduced or calcium sulfide is oxidized is the pressure of SO_2 observed along either the H_2-H_2O coexistence line (Fig. 13) or the CO-CO_2 coexistence line (Fig. 9). The same is true for S_2 pressures. The basis for these rather far-reaching conclusions is that in any process involving a reduction of calcium sulfate, the SO_2 and S_2 pressures will increase with increasing reducing ability of the atmosphere until calcium sulfide is formed. At that point, increasing the reducing ability of the atmosphere no longer increases the amount of SO_2 or S_2 formed, but rather causes the calcium sulfate to be transformed into calcium sulfide. Similarly, in a process in which calcium sulfide is oxidized, the SO_2 and S_2 pressures increase with increasing oxidizing ability of the atmosphere until calcium sulfate is formed. This point is again a limit, and SO_2 and S_2 pressures cannot be increased further.

3. Roasting of Calcium Sulfide

In the roasting process, calcium sulfide is oxidized with oxygen or air according to Eq. 16.

$$CaS + 3/2\ O_2 \rightleftarrows SO_2 + CaO \qquad K_p = \frac{P_{SO_2}}{\left(P_{O_2}\right)^{3/2}} \tag{16}$$

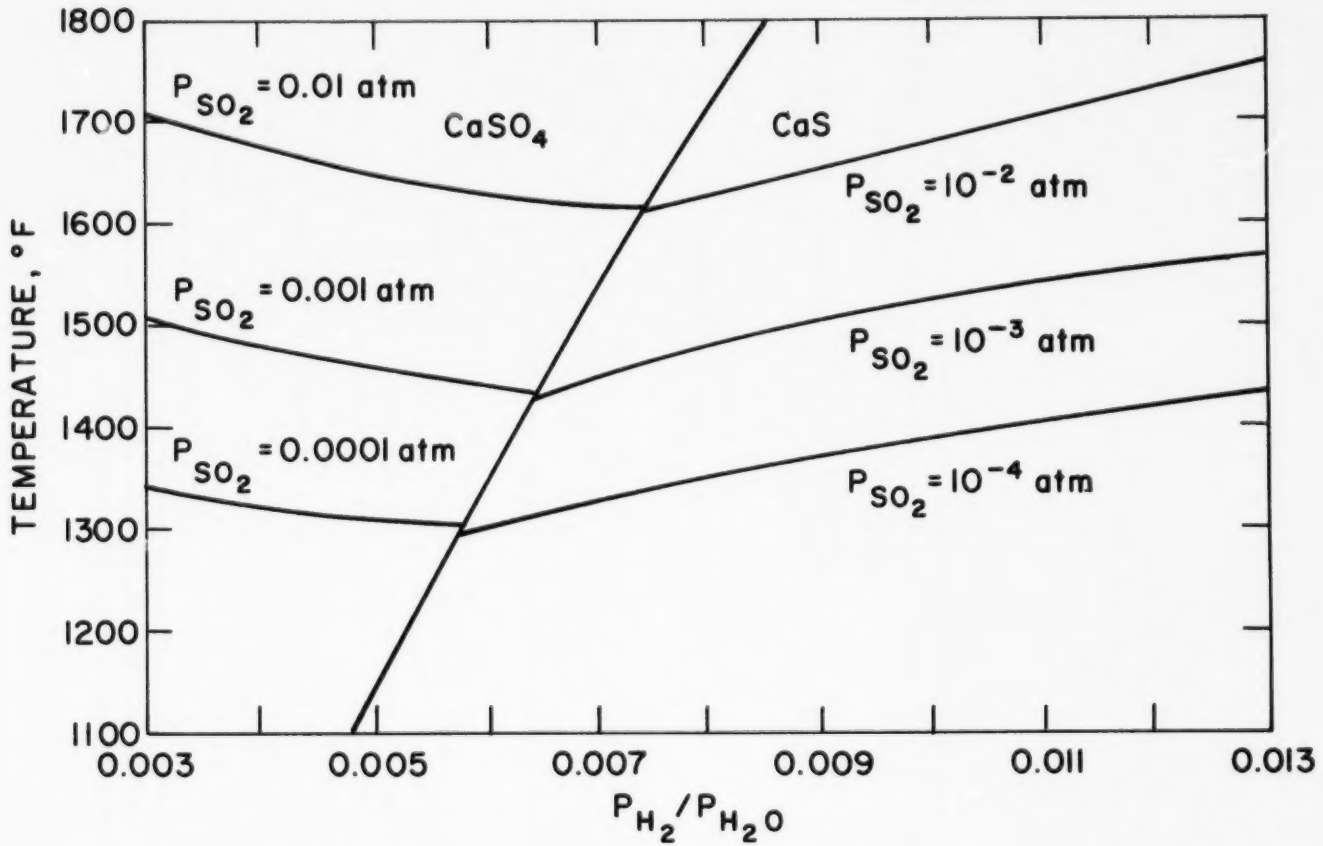

Fig. 13. Pressure of SO_2 in the $CaSO_4$-CaS-H_2-H_2O System

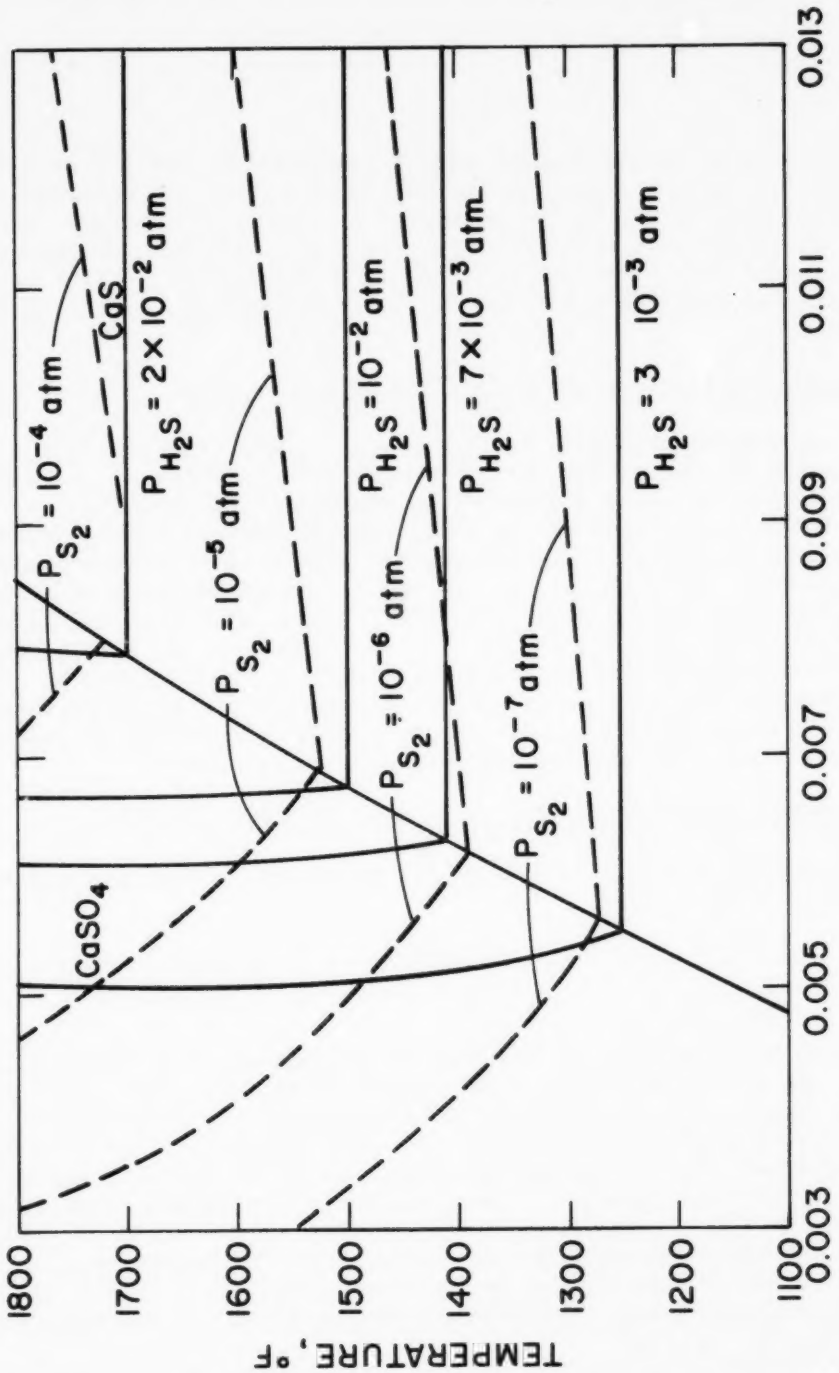

Fig. 14. S_2 and H_2S Pressures in the System S_2-H_2S-H_2-H_2O-$CaSO_4$-CaS

As may be seen by examining the equilibrium constant for Eq. 16, the pressure of SO_2 at any temperature increases with increasing pressure of oxygen. However, it follows from the arguments presented above that above some definite oxygen pressure (given at any temperature by K_p of Eq. 17),

$$1/2\ CaS + O_2 \rightarrow 1/2\ CaSO_4 \qquad K_p = \frac{1}{P_{O_2}} \tag{17}$$

calcium sulfide is no longer stable, but is converted to calcium sulfate. At this particular oxygen pressure, the SO_2 pressure is that observed along the coexistence line in the CO-CO_2 system or in the H_2-H_2O system. Thus, what appear to be two very different processes, the reductive decomposition of calcium sulfate and the roasting of calcium sulfide, are in fact very similar. Both processes give rise to identical maximum SO_2 pressures at a given temperature.

4. Pressure Effects in the CO/CO_2 and H_2/H_2O Systems

In all regeneration processes discussed above, the pressure of SO_2 is a function of the temperature or of the oxidizing ability of the atmosphere (in the case of the roasting and reductive decomposition processes). The pressure of SO_2 as a function of the total system pressure has not been discussed because SO_2 pressure is independent of the total system pressure in these processes. However, percent of SO_2 in the gas mixture is an inverse function of the total system pressure since the pressure of SO_2 is fixed at any temperature. The pressure of SO_2 is also independent of the presence of inert gaseous diluents if sufficient oxidizing or reducing gas is present. As stated above, in the case of reductive decomposition with CO-CO_2 mixtures, the presence of inert gases may affect the CO_2 pressure enough to change the reaction product from calcium carbonate to calcium oxide.

5. Acid-Base Reaction of Calcium Sulfide with H_2O and CO_2

Reaction 18 has been proposed as a regeneration reaction for calcium sulfide.

$$H_2O + CO_2 + CaS \rightleftarrows CaCO_3 + H_2S \qquad K_p = \frac{P_{H_2S}}{P_{CO_2} P_{H_2O}} \tag{18}$$

Calcium sulfide is formed in the additive by (1) burning coal in a fluidized bed of limestone or dolomite with a deficiency of air or by (2) reducing the $CaSO_4$ in additive from a run in which combustion was with an excess of air. Unlike all other regeneration reactions discussed here, this reaction is pressure-sensitive. The percentage and the pressure of H_2S increase with increasing total system pressure. The pressure of H_2S is also sensitive to the presence of inert-gas diluents, in contrast to the previously mentioned regeneration schemes. The equilibrium constant for this exothermic reaction becomes smaller as the temperature is increased (Fig. 15). This is in direct contrast to the other (endothermic) regeneration schemes mentioned.

Maximum H_2S yield is obtained when the H_2O/CO_2 ratio in the feed gas is 1 to 1, as may be seen by an examination of the equilibrium constant

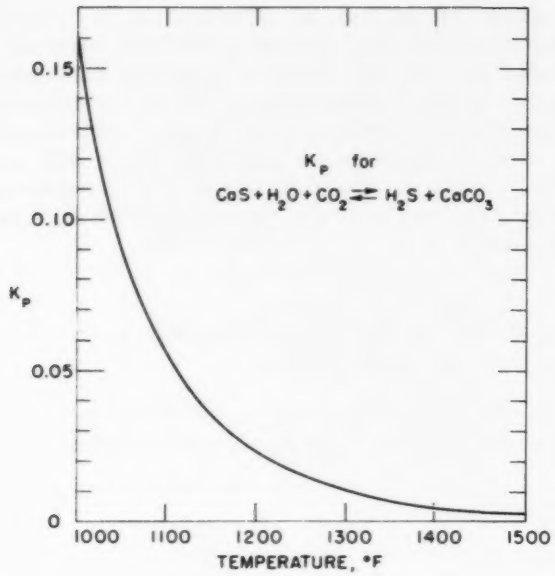

Fig. 15. Equilibrium Constant as a Function of Temperature, $CO_2 + H_2O + CaS \rightarrow CaCO_3 + H_2S$

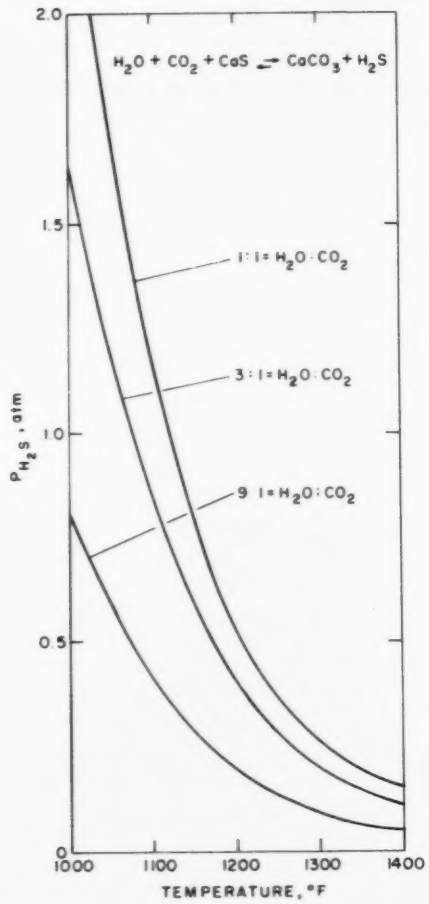

Fig. 16. Pressure of H_2S in Undried Gas Stream as a Function of Temperature at 10-atm P_{total}

expression. Figure 16 shows the pressure of H_2S as a function of temperature, assuming 10-atm total pressure and an inlet gas stream composed only of H_2O and CO_2 at various ratios. However, H_2O may be readily removed from the product gas stream by condensation. Thus, higher values of H_2S concentration in a dried gas stream may be obtained by operating with higher ratios of H_2O/CO_2 in the inlet gas stream. For an inlet gas composition of 50% water and 50% CO_2 and temperatures of 1000-1400°F, Table 8 gives the percentage of H_2S in the gas effluent from the reactor and the percentage of H_2S in the same effluent after it has been dried.

TABLE 8. H_2S Concentration[a] in Dried and Undried Product Gas Stream at Equilibrium

Temp (°F)	% H_2S in Undried Gas	% H_2S in Dried Gas
1000	23.0	37.4
1100	11.4	20.5
1200	4.7	9.9
1300	2.7	5.1
1400	1.4	2.8

[a]Assumptions are 10-atm total pressure and an inlet gas of 50% H_2O and 50% CO_2.

B. Experimental Studies

1. Reductive Decomposition of $CaSO_4$

To test the accuracy of the equilibrium compositions calculated for the reduction of $CaSO_4$ with CO/CO_2 mixtures, experiments have been performed in a static system. The apparatus (shown in Fig. 17) consists of a horizontal tube reactor fabricated from recrystallized alumina. The tube is 36 in. long and has an ID of 3 in. with 1/4-in. walls. One end of the alumina reactor is closed, and the opposite end is capped with a stainless steel O-ring flange. There are openings in the flanged end (which is outside the furnace) for gas lines and the thermocouple well.

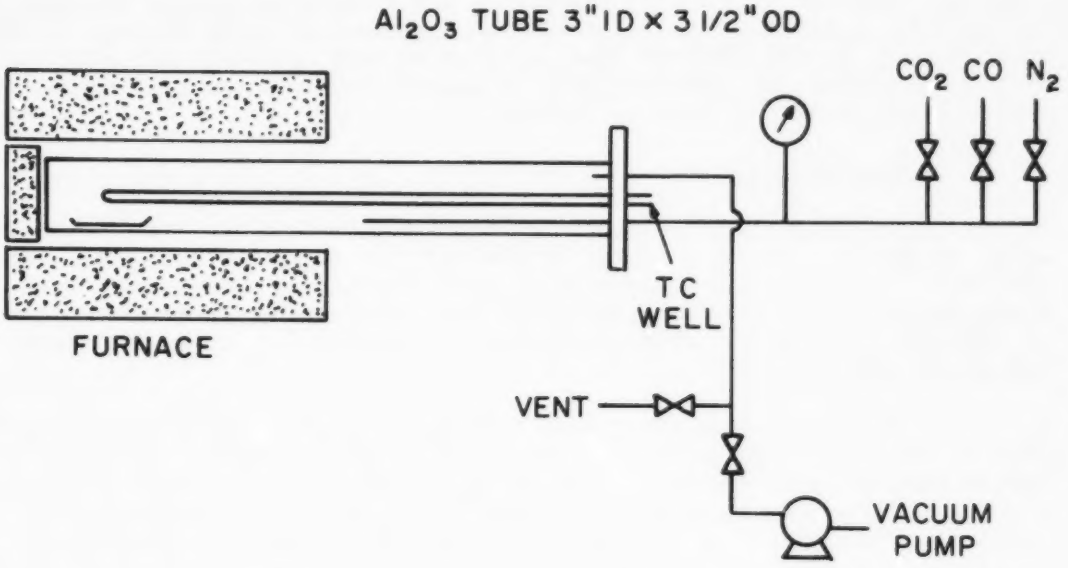

Fig. 17. Schematic of Apparatus for Equilibrium Measurements on $CaSO_4$-CO/CO_2 System

The experiments were performed in the following manner. A 3-g sample of $CaSO_4$ (Drierite) was placed in an alumina boat and loaded into the reactor. The system was closed and leak-checked, and the $CaSO_4$ was dried at 500°F under vacuum for 15-20 hr. While the system was still at 500°F and isolated from the vacuum pump, a predetermined pressure (<1 atm) of CO was added. The total pressure of the system was then increased to 1 atm by adding CO_2. The system was allowed to stand for 30 min; then a gas sample was taken through a septum in the flange using a hypodermic syringe. The gas sample was analyzed for CO by gas chromatographic techniques.

Next, the pressure of the system was reduced to 400 mm Hg and the temperature was increased to 1900°F, increasing the pressure to ~1 atm. With the system at 1900°F, samples of the gas mixture were obtained at selected

intervals and analyzed for CO and SO_2. After the final gas sample was obtained, the system was flushed with nitrogen to remove reactant and product gases. The temperature was lowered to room temperature, and the residue in the alumina boat was removed and analyzed for Ca, total S, and $S^=$ by wet chemical analytical techniques.

Experimental results presented in Fig. 18 show good agreement, in most cases, between experimental and calculated values of SO_2 levels when $CaSO_4$ was reacted with CO/CO_2 over a range of ratios. Other data indicate that CO and SO_2 were being slowly removed by a secondary process. Analyses of the gas samples indicate that reaction was occurring in the ratio of one mole of SO_2 to one mole of CO, forming one mole of CO_2 during the period of equilibration at 1900°F (the other reaction product was probably elemental sulfur, which was found at the cooler end of the alumina tube). This secondary reaction, evident in those runs in which the equilibration time was very long (∿20 hrs) and/or the CO/CO_2 ratio was high, caused the points to fall off the equilibrium line. In an experiment in which SO_2 was diluted with N_2 only, it was observed that SO_2 reacted with materials of construction to a small extent; SO_2 concentration decreased from 15% initially to 14% in 2 hr and to 13% in 20 1/2 hr at 1900°F.

2. Two-Step Process

A second regeneration procedure of interest is to first reduce the $CaSO_4$ to CaS and then to make H_2S by the reaction of CaS with H_2O-CO_2. Experimental data on these process steps were obtained in a 2-in.-dia batch fluidized-bed reactor. The regenerator and associated equipment are shown in Fig. 19. The reactor system consisted of the reactor, a gas preheater, and an off-gas filter.

The reactor was fabricated from Type 316 SS. Solids can be removed from the fluidized bed in the reactor during an experiment by evacuating a solids receiver tube and then transporting the solids to the tube by opening a valve between the higher pressure reactor and the tube. Heating of the reactor and preheater was done electrically. The pressure of the reactor system was controlled by a pressure transmitter, pneumatic controller, and a pneumatic valve. Analysis of the effluent gas was performed with infrared analyzers, a gas chromatograph, and a quadrupole mass spectrometer.

The bed material consisted of either $CaSO_4$ (Drierite) or partially sulfated dolomite or limestone obtained from the coal combustion experiments. Nitrogen and carbon dioxide were obtained from the evaporation of the liquids or from cylinder sources. The other reactant gases were obtained from the cylinder sources.

a. Conversion of $CaSO_4$ to CaS (Reduction Step). The effect of temperature on the rate of reduction of $CaSO_4$ to CaS with hydrogen was studied and is shown in Figs. 20 and 21. The additive used was partially sulfated dolomite ($CaSO_4$/CaO/MgO, 15.4 wt % Sulfur) obtained in an earlier experiment in which the dolomite (obtained from Charles Pfizer Co., Gibsonburg, Ohio) took up SO_2 during combustion of coal at 1550°F. In the H_2-reduction runs, the gas velocity was ∿6 ft/sec and the system was at atmospheric pressure. Approximately three stoichiometric equivalents of

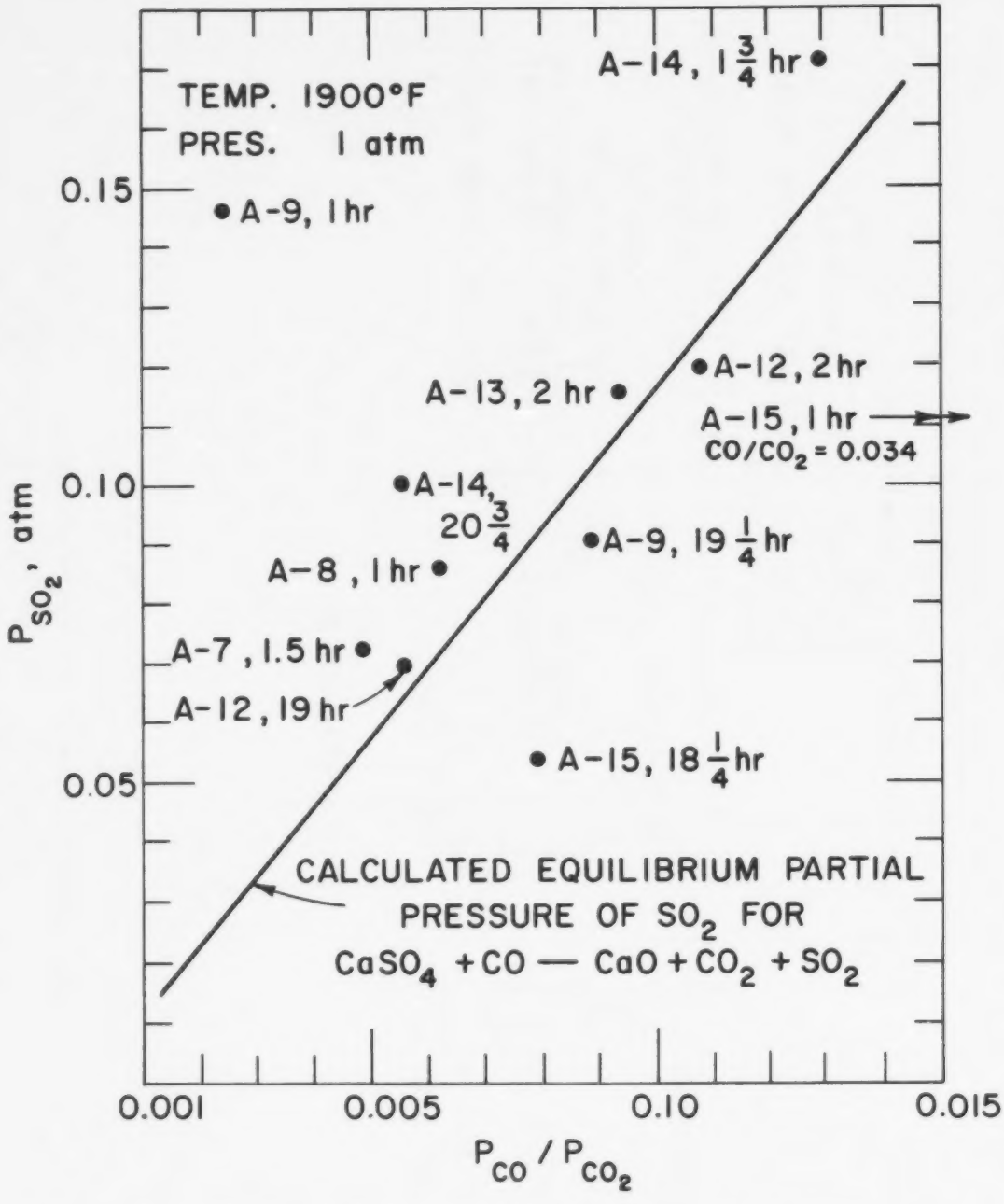

Fig. 18. Experimental and Calculated Partial Pressures of SO_2 Over a Range of P_{CO}/P_{CO_2} Ratios
(Temp: 1900°F; total pressure: 1 atm)

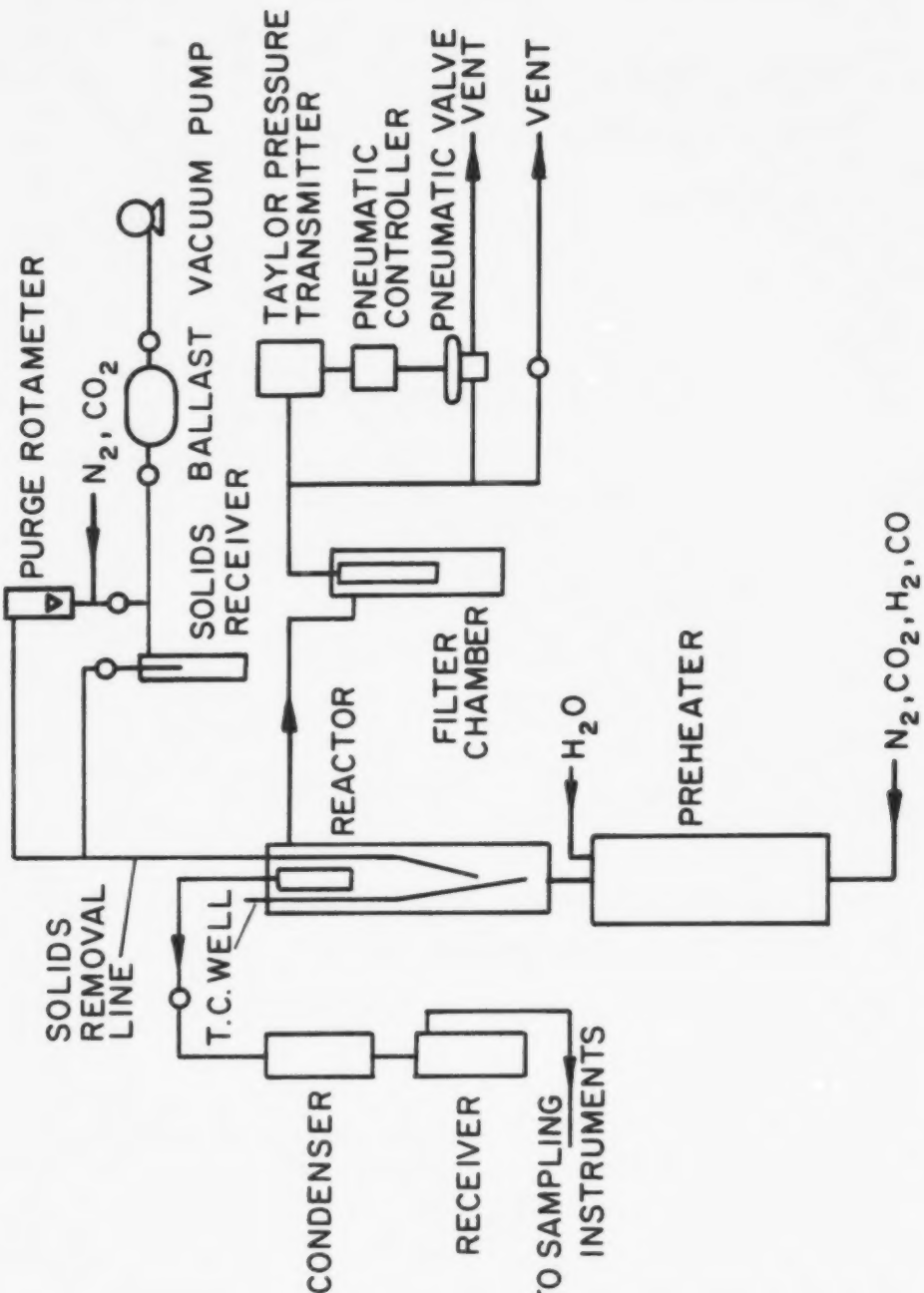

Fig. 19. Two-Inch-Diameter Fluidized-Bed Reactor

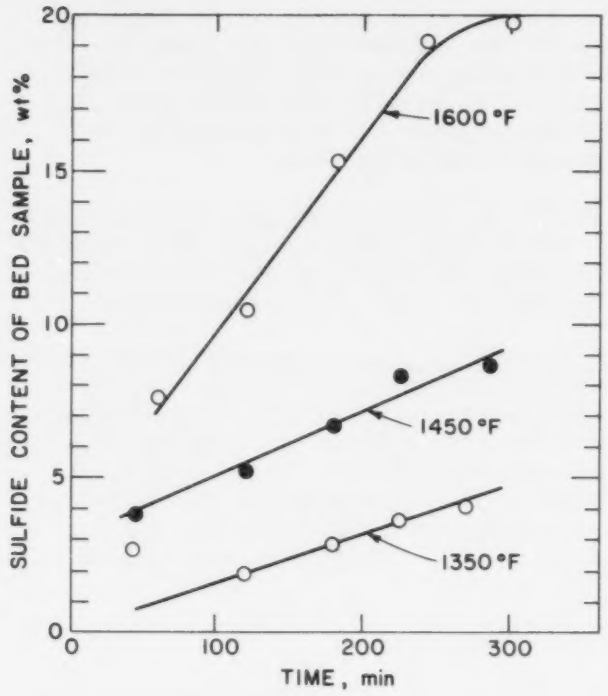

Fig. 20. Sulfide Content of Bed during Reduction of Partially Sulfated Dolomite with Hydrogen at Various Temperatures

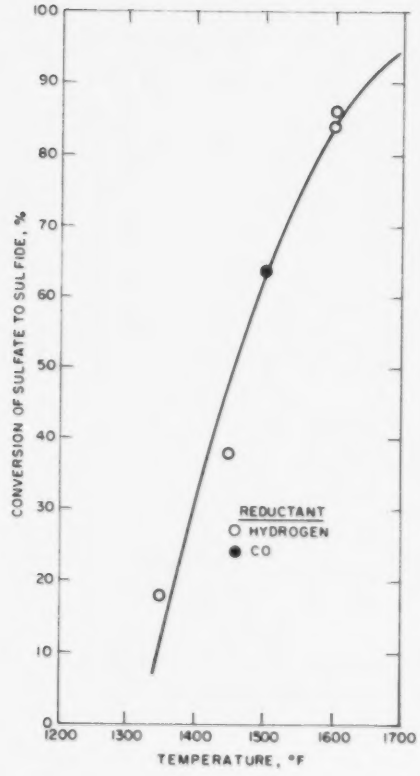

Fig. 21. Effect of Temperature on Reduction of $CaSO_4$ (Dolomite) (4.5-hr reduction time; 1-atm pressure)

pure hydrogen were added over the 5-hr period of the runs. As would be expected, the sulfide concentration in the bed material was lower at 1350°F than at either 1450°F or 1600°F after equivalent reaction times. Percent conversions after 4.5 hr at 1350°F, 1450°F, and 1600°F were 18%, 38%, and 86%, respectively. If all the sulfate had been converted to sulfide, the sulfur content of the sample would be ∿21%.

Since in practice, CO may be the reducing gas, an additional experiment was performed with CO. The percent reductions of $CaSO_4$ with CO and the expected reduction using H_2 (Fig. 20) agreed at the temperature employed (1500°F); however, this may not be true at all temperatures.

b. Reaction of CaS with CO_2/H_2O (Regeneration Step). The product of each of the reduction experiments was carbonated at 10 atm with CO_2 to simulate a product that would be obtained in an actual 10-atm combustion-reduction experiment. This material was then reacted batchwise with an equimolar mixture of CO_2/H_2O at temperatures ranging from 900 to 1100°F, a gas velocity of approximately 1 ft/sec, and 10-atm pressure in the 2-in.-dia fluidized-bed reactor. The H_2S concentration in the outlet gas was monitored with a quadrupole mass spectrometer. Conditions and results of the experiments are shown in Table 9.

The results to date have shown that:

1. The reaction producing H S was initially rapid, but the rate decreased after a short time. Typically, the reaction rate dropped nearly to zero after several minutes (Fig. 22).

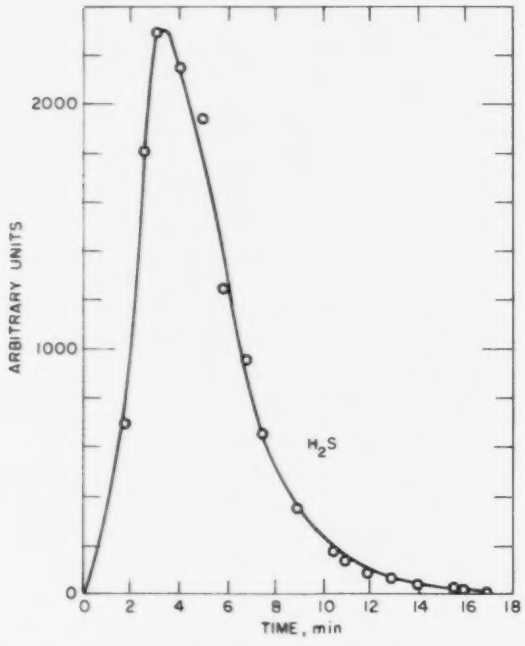

Fig. 22. Typical H_2S Levels in the Outlet Gas for CO_2/H_2O Regeneration

TABLE 9. Regeneration Experiments, Conditions and Results

Reactor: 2-in.-dia batch reactor
Reactor Pressure: 10 atm

Experiment No.	Conditions and Reductant for Preparation of Material for Regeneration Step*					Regeneration Step**					H_2S Concentration, %	
						Starting Bed			Ending Bed			
	Reductant	Temp., °F	Stoichiometric Equivalents Added	Gas Velocity, ft/sec	Time, hr	$S^=$, %	S, %	Temp., °F	$S^=$, %	S_T, %	Peak	Equil.
CATS-17	100% H_2	1600		0.7	4.7	17.7	20.4	1000	9.5		37	37.4
-18	100% H_2	1450			4.7	8.7		900			43.6	59.0
-19	100% H_2	1350		0.6		4.1		1100	2.3	15.0	11.2	20.5
-20	100% CO	1500	1.7	0.16 0.40	2.7 2.0	12.2	19.1	1000	5.3		35.5	37.4
-21	85% CO/ 15% CO_2	1600	5.0	1.0	5.0	6.1		1000	2.8		37.2	37.4

*Starting material was dolomite from Charles Pfizer Co. which had been sulfated in the 6-in.-dia fluidized bed combustor at 1550°F. The sulfated dolomite contained 15.4 wt % sulfur. Reactor pressure during reduction step was 1 atm.

**Reactor pressure was 10 atm. Reactant gas velocity was 1.3 ft/sec.

2. The peak concentration of H_2S in the outlet gas was high, near the expected equilibrium value.

3. Typically, half or less of the CaS reacted.

In continuing work, the effects of process variables are being studied in an attempt to increase the quantity of CaS reacted.

c. Sulfation-Regeneration Cyclic Experiments. Since it will be desirable to reuse the additive material several times in commercial applications, a cyclic experiment has been performed to obtain data on the pick-up and removal of sulfur from additive particles and to determine decrepitation and attrition of additive particles during sulfation-regeneration cycles. Six cycles of simulated combustion and two-stage regeneration were performed with a single bed of additive. The starting material (1.2 kg) was the final bed from a coal combustion experiment in which dolomite No. 1337 had been used as additive. The initial sulfur content of this material was 15.4 wt %. The experiment was performed batchwise in the 2-in.-dia fluidized-bed reactor. Data on operating conditions and sulfur analysis of the products of each step are shown in Table 10.

The sulfation portion of cycle 1 was omitted since the additive already contained sulfur. For the remaining cycles, the constituents of the synthetic combustion gas were N_2, CO_2, H_2O, O_2, CO, and SO_2. The sulfation reaction was allowed to proceed until the bed material had essentially ceased further pickup of SO_2. After the bed had been sulfated, the $CaSO_4$ was converted to CaS, using H_2 or CO as reductant at 1550 to 1600°F and 10 atm. The bed was then reacted with a CO_2/H_2O gas mixture at 1000°F and 10 atm to convert the CaS to $CaCO_3$. A sample of the bed material was taken after each step in the cycle and analyzed for sulfur and sulfide content.

The effluent gas stream was analyzed for H_2S concentration, using the quadrupole mass spectrometer. A plot of H_2S concentration vs reaction time for each of the six cycles is presented in Fig. 23.

The results (see Table 10) for the sulfation cycles indicate an increase in sulfur content with each succeeding cycle except between the fourth and fifth cycles. It is not possible, however, to determine if this means an actual increase in total sulfur content since the weight of the bed after each cycle is unknown.

The results indicate that the conversion of $CaSO_4$ to CaS in the reduction step was ineffective. Only in cycles 1 and 4 was the conversion to CaS greater than 50%. A possible cause is the interaction of $CaSO_4$ and CaS to form nonporous surfaces; the formation of easily sinterable cakes has been reported when CaS-$CaSO_4$ are present.[4]

The data for the regeneration step indicate that the peak concentrations of H_2S in the effluent gas decreased from 13 vol % (dry basis) for cycle 1 to 0.5 vol % (dry basis) for cycles 5 and 6. Equilibrium concentrations of H_2S would have been ~25%. The percent sulfide converted to CaO or $CaCO_3$ decreased from 9.7% to a very low indeterminant value.

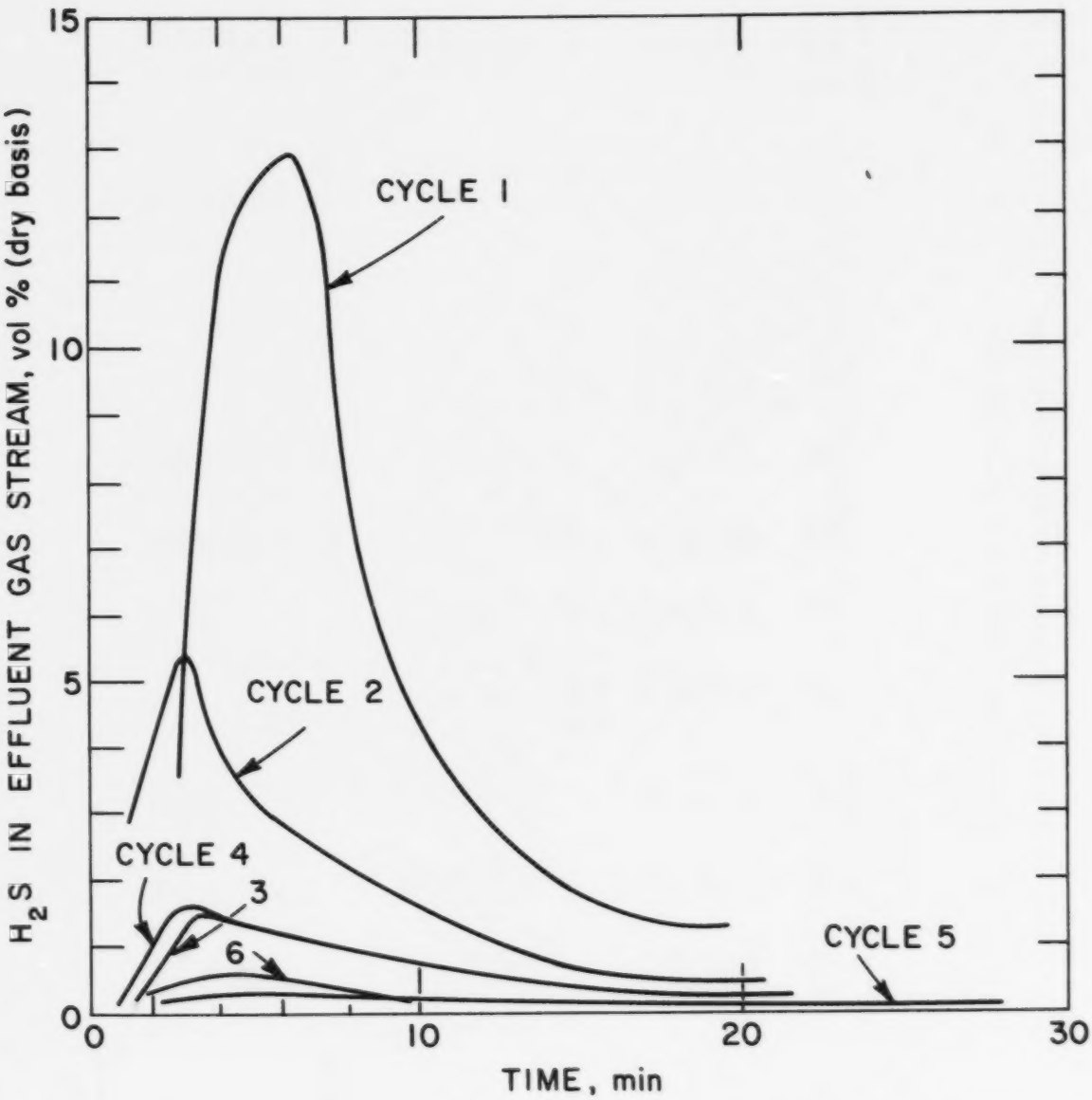

Fig. 23. H_2S Concentration in Effluent Gas Stream in Regeneration Step

TABLE 10. Conditions for Cyclic Experiment

Starting Bed: 1200 g of Sulfated Dolomite
Final Bed: 561 g

Sulfation Cycle	T, °F	P, atm	Time, hr	Gas Flowrate, cfh (10 atm, 70°F) N_2	CO_2	H_2O	O_2	CO	SO_2	Total	Gas Vel., ft/sec, at T.P.	Analytical Results for Bed Sample S_{Total}, wt %	$S^=$, wt %
1												15.4	-
2	1500	10	~2	24	12	23	1.5	0.1	0.5	61.0	2.9	16.4	-
3	1500	10	2	24	12	23	1.5	0.1	0.5	61.0	2.9	17.8	-
4	1500	10	1.5	24	12	23	1.5	0.1	0.5	61.0	2.9	18.0	-
5	1500	10	1	24	12	23	1.5	0.1	0.5	61.0	2.9	16.7	-
6	1500	10	2	24	12	23	1.5	0.1	0.5	61.0	2.9	N.S.	-
Reduction Cycle				H_2	CO	CO_2	N_2			Total			
1	1550	10	4.5	5.7	-	5.0	6.0			16.7	0.8	20.8	15.5
2	1550	10	4.5	5.7	-	1.2	3.0			9.9	0.47	20.8	9.2
3	1550	10	4.5	-	4.1	1.8	0.5			6.4	0.31	16.6	7.6
4	1600	10	5.5	-	5.1	0.7	3.0			8.8	0.44	18.7	13.9
5	1600	10	5.0	-	5.1	0.7	3.0			8.8	0.44	16.8	5.9
6	1600	10	5.0	5.7	-	0.7	-			6.4	0.32	N.S.	N.S.
Regeneration Cycle			Time, min			CO_2	H_2O			Total			
1	1000	10	20			18	18			36	1.37	18.9	14.0
2	1000	10	21			18	18			36	1.37	18.8	8.4
3	1000	10	21			18	18			36	1.37	17.7	6.8
4	1000	10	21			18	18			36	1.37	19.6	14.8
5	1000	10	30			18	18			36	1.37	18.2	6.0
6	1000	10	26			18	18			36	1.37	15.5	2.0

N.S. - No sample.

The sulfur contents in the initial and final beds were 15.4 and 15.5 wt %, respectively. The weights of sulfur in the initial and final bed were 185 g and 87 g, respectively. A portion of the 98 g of sulfur not accounted for in the bed was in bed samples. The total weight of bed samples was about 200 g, possibly containing ~34 g of sulfur.

To obtain information on physical changes that occurred in additive material during sulfation-regeneration cycling, a microscopic examination was performed on additive material from the initial bed, bed material sampled after the third cycle regeneration, and final bed material. Photographs of particles are presented in Figs. 24 and 25.

It is apparent from the photographs that with additional recycling, the layer of material on the surface of the particles becomes thicker, probably by diffusion into the particle rather than by buildup of material on the surface. The mechanism for layer formation is not known at present but may be solid solution formation. A more detailed microscopic examination of this material will be performed, and hopefully the composition of the layer will be determined.

The photographs also indicate that the porosity of the particles may increase slightly as recycling proceeds.

To obtain data on the amount of attrition and agglomeration of additive material during several cycles of sulfation-regeneration, a particle size analysis was performed on starting bed material and final bed material from the cyclic experiment. The data (presented in Table 11) indicate that there was only slight agglomeration or attrition in six cycles of sulfation-regeneration.

d. Sulfiding-Regeneration Experiments. Because the presence of $CaSO_4$ might have contributed to the poor sulfur removals noted in the sulfation-regeneration experiments, several sets of cyclic experiments with dolomite or limestone starting beds were performed in which $CaCO_3$ was reacted directly with H_2S and then the product CaS was reacted with CO_2/H_2O. The MgO in the dolomite bed was calcined before the H_2S reaction. Preliminary experimental results from data available show that:

1. The regeneration reaction was initially rapid, but the reaction rate decreased after a short time, the same as when $CaSO_4$ was present.

2. The peak concentration of H_2S in the outlet gas during regeneration was near the expected equilibrium value in the first cycle.

Experimental work is continuing, data are being evaluated, and particles are being examined by different techniques to gain an insight into the reaction mechanism.

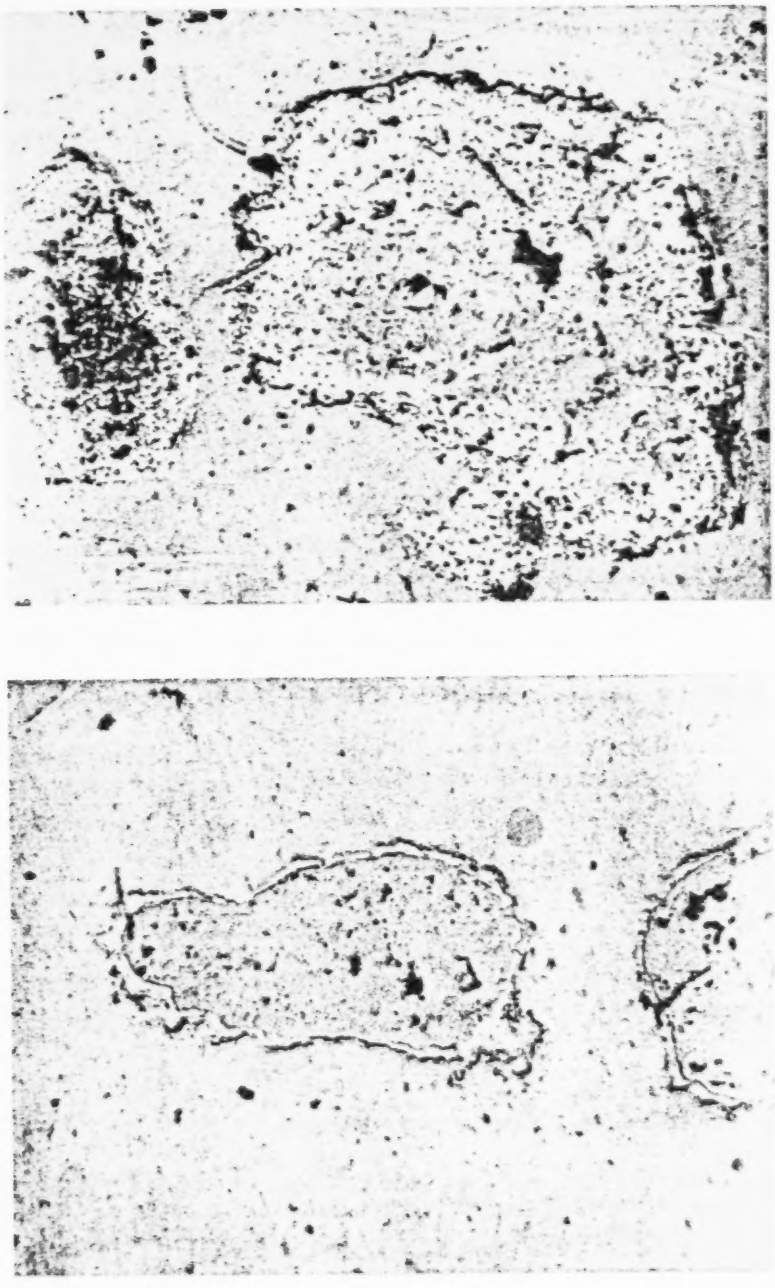

Fig. 24. Photomicrographs Showing Cross Sections of Particles from Cyclic Experiment (X100)

Fig. 25. Photomicrograph Showing Cross Sections of Particles from Cyclic Experiment X100

TABLE 11. Sieve Size Analysis of Starting Bed and Final Bed After Six Cycles

U.S. Mesh Size	Starting Bed, wt %	Final Bed, wt %
+25	2.0	11.0
-25+40	54.0	45.6
-40+60	36.4	34.6
-60+80	6.5	6.2
-80+100	0.6	1.0
-100+230	0.3	0.8
-230	0.1	0.8
TOTAL	100.0	100.0

V. PRESSURIZED COMBUSTION AND REGENERATION PILOT PLANT

A. Description

Equipment has been installed for combusting coal at pressures up to 10 atm and for regenerating sulfated lime for reuse. A simplified equipment schematic is shown in Fig. 26.

The solids feeders are of the rotary pocket type, equipped with hoppers which are loaded batchwise.

The gas preheater (see Fig. 27) was designed in accordance with ASME code requirements, and its design rating is 150 psig at 1500°F. Air (or gas) passes through an annulus, reverses direction, and passes through a central section containing electrical heaters.

The regenerator and the fluidized-bed combustor, which have a common preheater and off-gas system (cyclones, filters, gas-sampling equipment, pressure let-down valve, and scrubber), will not be operated simultaneously. When the combustor or the regenerator is in operation, the other unit will be disconnected from the off-gas line and flanged off.

The combustion unit (see Fig. 28) consists of a 6-in. schedule 40 pipe (Type 316 stainless steel) approximately 11 ft long, with an outer shell consisting of 12-in. schedule 10 pipe (Type 304 stainless steel) over nearly the entire length. A bellows expansion joint is incorporated into the outer shell to accommodate the differential thermal expansion of the inner and outer vessels.

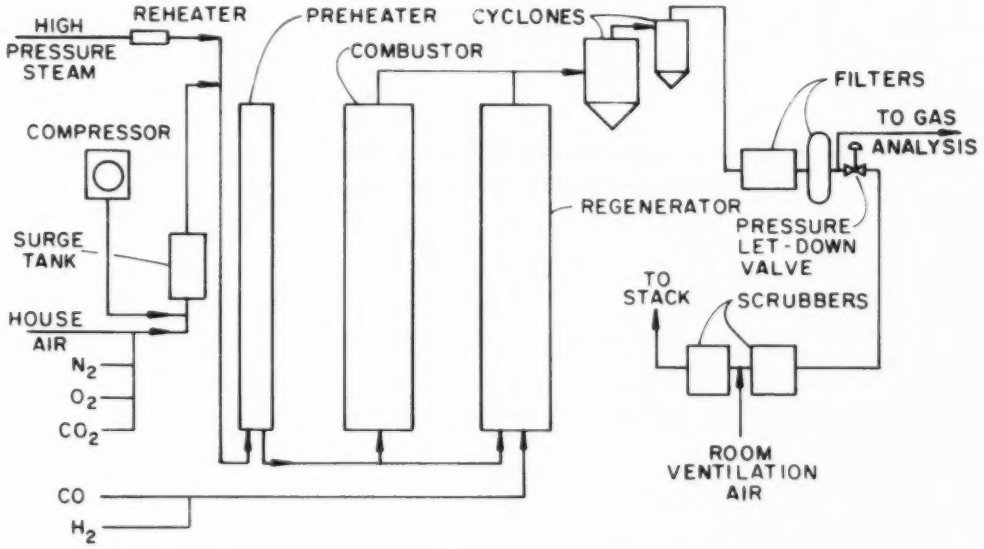

Fig. 26. Simplified Schematic of Pressurized Combustion-Regeneration Equipment

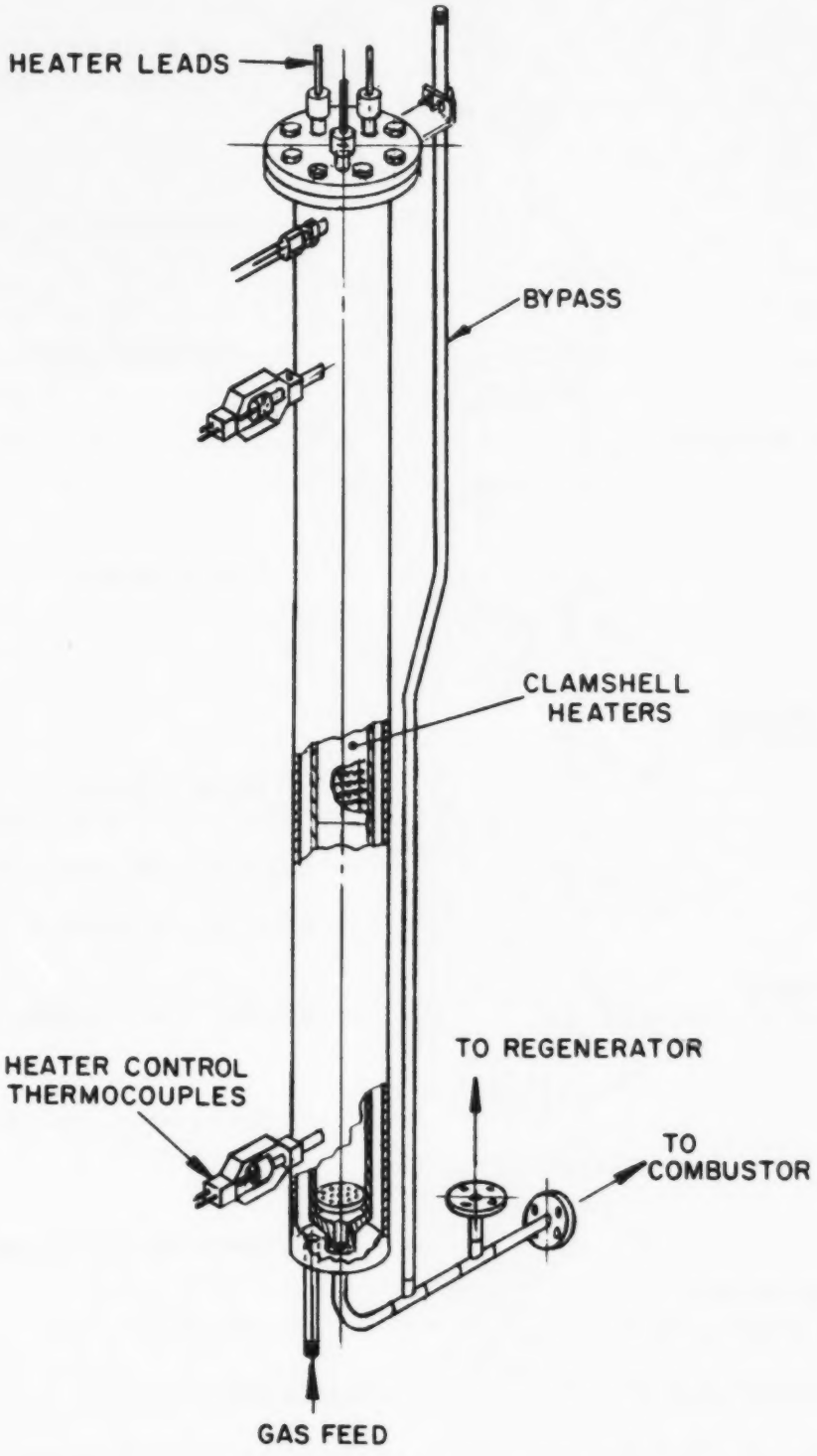

Fig. 27. Six-inch Fluidizing Gas Preheater.
ANL Neg. No. 308-3368.

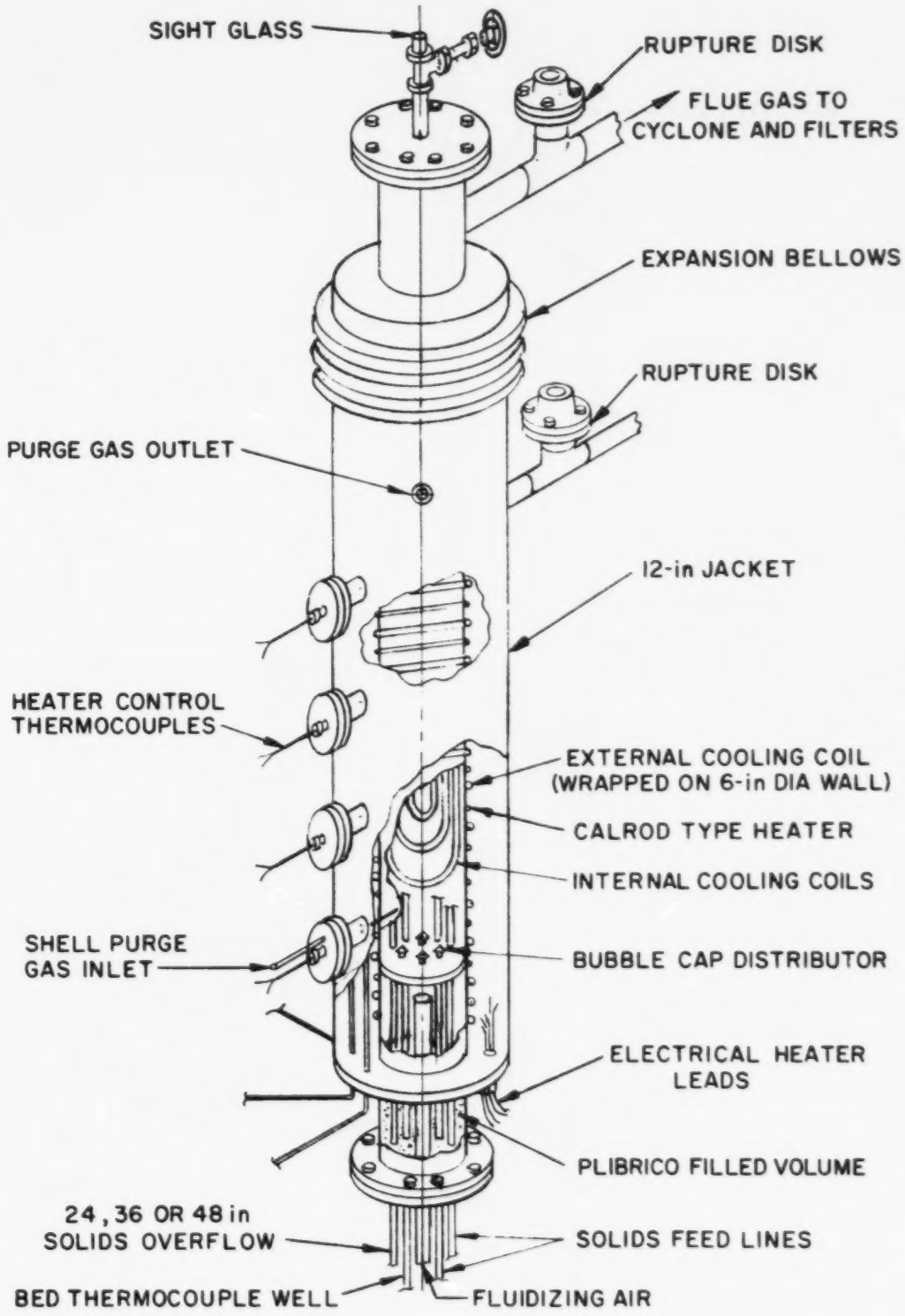

Fig. 28. Six-inch Dia Pressurized Fluidized-Bed Combustor.
ANL Neg. No. 308-3366.

The unit is of a balanced-pressure design, i.e., the annular chamber between the two pipes is maintained under pressure so that there is no differential pressure across the hot inner-pipe wall. The balancing pressure for the shell is supplied by a bank of nitrogen cylinders.

A bubble-cap-type gas distributor is flanged to the bottom end of the combustor inner vessel; thermocouples, solids feed lines (coal and additive are injected upward into the bed through a 45° angle tube) and solids take-off lines extend through the gas distributor. The outer wall of the 6-in. pipe is wrapped alternately with sixteen 3000-W tubular resistance heaters and 3/8-in.-OD cooling coils that are spray-metal-bonded. Internal cooling coils of 3/8-in. pipe extend down into the interior of the 6-in. vessel from the flanged top to provide additional heat transfer area. Water flow to the cooling coils is regulated with flow indicators and is adjusted to obtain the selected temperatures of the fluidized bed and reactor wall.

Both the annular pressure chamber and the reactor itself are equipped with rupture disc assemblies and pressure relief valves vented to the room-ventilation exhaust ducts.

The regenerator (see Fig. 29) has a 3-in. ID. It consists of a 2 1/2-in. Plibrico castable refractory encased in an 8-in. schedule 40 pipe (Type 316 stainless steel). This entire assembly is enclosed in a pressure shell made of 12 in., schedule 20 carbon steel pipe. Differential thermal expansion between the inner and outer pipes is accommodated by using packing glands on the lines entering the bottom flange of the unit. The unit is of a balanced-pressure design. The balancing gas is nitrogen. Since the annular space is not gas-tight with respect to the regenerator inner vessel, the pressure in the annular space will be maintained slightly higher than the regenerator pressure to prevent process gases from entering the annulus. A pressure alarm gauge will monitor the pressure in the annular space and will be set to warn of both high and low pressures.

A bubble-cap type gas distributor is connected to the bottom of the inner regenerator vessel via a slip fit and held in place with retaining screws. Thermocouples, solid feed lines, and solids take-off lines pass through the gas distributor and through packing glands on the bottom flange of the outer pressure vessel. The wall of the inner vessel is wrapped alternately with 3000-W tubular resistance heaters and 3/8-in.-OD cooling coils. Both the annular chamber and the regenerator itself are equipped with rupture disc assemblies and pressure relief valves vented to the room ventilation exhaust ducts.

The primary-filter cartridges (epoxy-impregnated cellulose-base material with glass fiber substrate) are suitable for gas temperatures up to 350°F. The secondary-filter cartridges are Rigimesh (woven metal wire).

Testing of the combustor and regenerator has started.

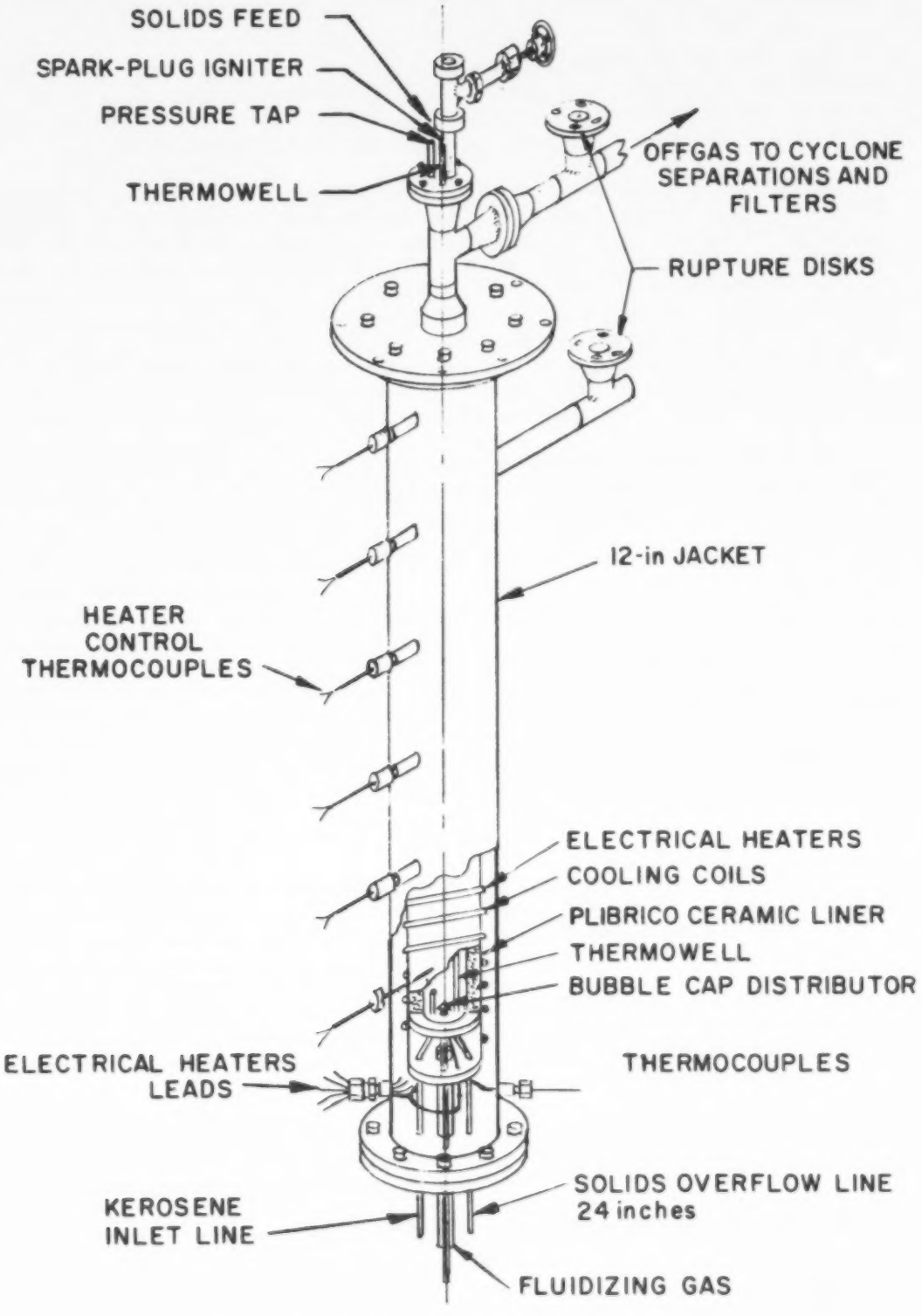

Fig. 29. Three-inch Dia Fluidized-Bed Regenerator.
ANL Neg. No. 308-3367.

B. Petrocarb Solids Feeder Tests

A modified Petrocarb solids feeder was tested for its suitability in feeding coal, limestone, or mixtures of coal and limestone to a pressurized bench-scale combustor-regenerator. Uniform feed rates in the range of 20 to 100 lb/hr are required in the high-pressure combustion system.

A facility consisting of a feeder, a transport line, and a solids collection system was constructed for testing the evenness and reproducibility of feeding the solids. The main features of the feeder (see Figs. 30 and 31) are a conical-bottom tank (that contains solids) and a mixing valve assembly to mix the solids with the carrier gas. The solids in the tank are aerated by a controlled stream of air at a selected pressure. In a test, the aerated solids flowed down from the conical bottom through an orifice in the mixing valve assembly into a controlled stream of air and were pneumatically conveyed through a transport line to a solids receiving vessel that contained a solids filter. For our use, a 1/4-in. orifice mixing-valve assembly was selected that was projected to give solids flows as low as 20 lb/hr.

The solids feed rate was controlled by two factors--air pressure in the tank and the total air flow rate. The tank pressure was controlled by adjusting the tank pressure regulator; the gas flow rate was regulated by adjusting a control valve until the prescribed flow was indicated on the flowrator.

Eighteen exploratory runs were made with -8 mesh limestone at feed rates of 11 to 300 lb/hr. Tank pressure, except for one run at 70 psig, was less than 20 psig. At feed rates much lower than 60 lb/hr, limestone flow was neither reproducible nor continuous. This was unsatisfactory since limestone feed rates of 20 to 40 lb/hr are required in bench-scale development studies.

Nine exploratory runs were made with -14 mesh coal--five at atmospheric pressure and four at above-atmospheric pressure (~80 psig). After feeding of the coal was started, it was observed in each of the runs that during an initial period of short duration (<10 min), the coal feed rates either increased gradually or fluctuated widely before reaching a steady-state period of long duration. The average coal feed rates during the steady-state periods for the five runs at atmospheric pressure in the receiving vessel ranged from 31.6 to 45.7 lb/hr. The air flow rates ranged from 1.29 to 2.67 scfm. The maximum deviations of feed rates from the average values were approximately ±15%, similar to those observed previously with limestone. In the four above-atmospheric experiments, the average coal feed rates ranged from 97.8 to 179.3 lb/hr and the air flowrates from 2.21 to 3.27 scfm.

Another set of tests was made at 76-85 psig to determine if uniform feed rates lower than the minimum previously obtained in high-pressure operation could be achieved by modifying the equipment and/or using coal with different properties. The equipment modifications investigated in this work were orifice diameter and length of the transport line. The coal properties studied were particle size distribution and moisture content.

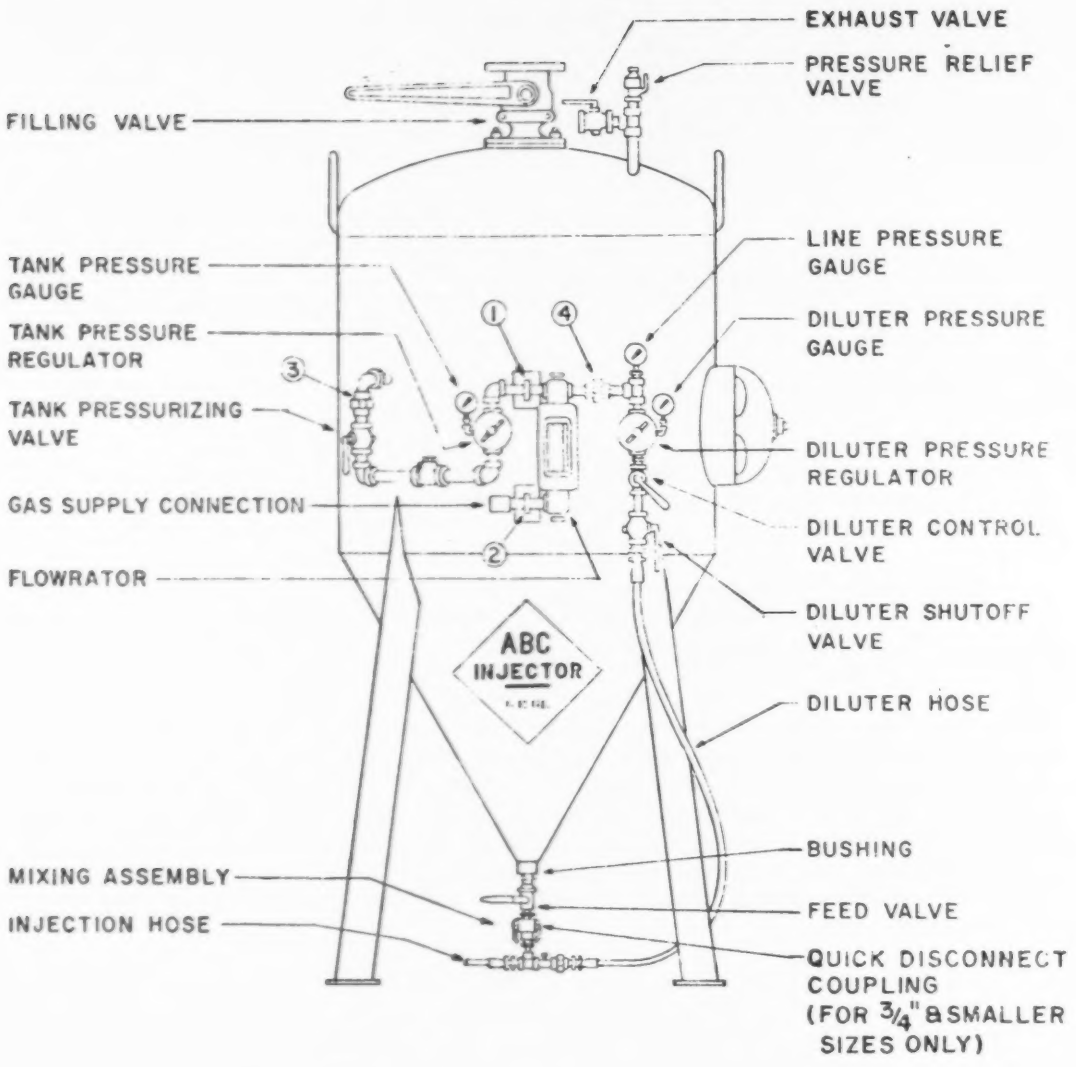

Fig. 30. Model 16 ABC Petrocarb Injector

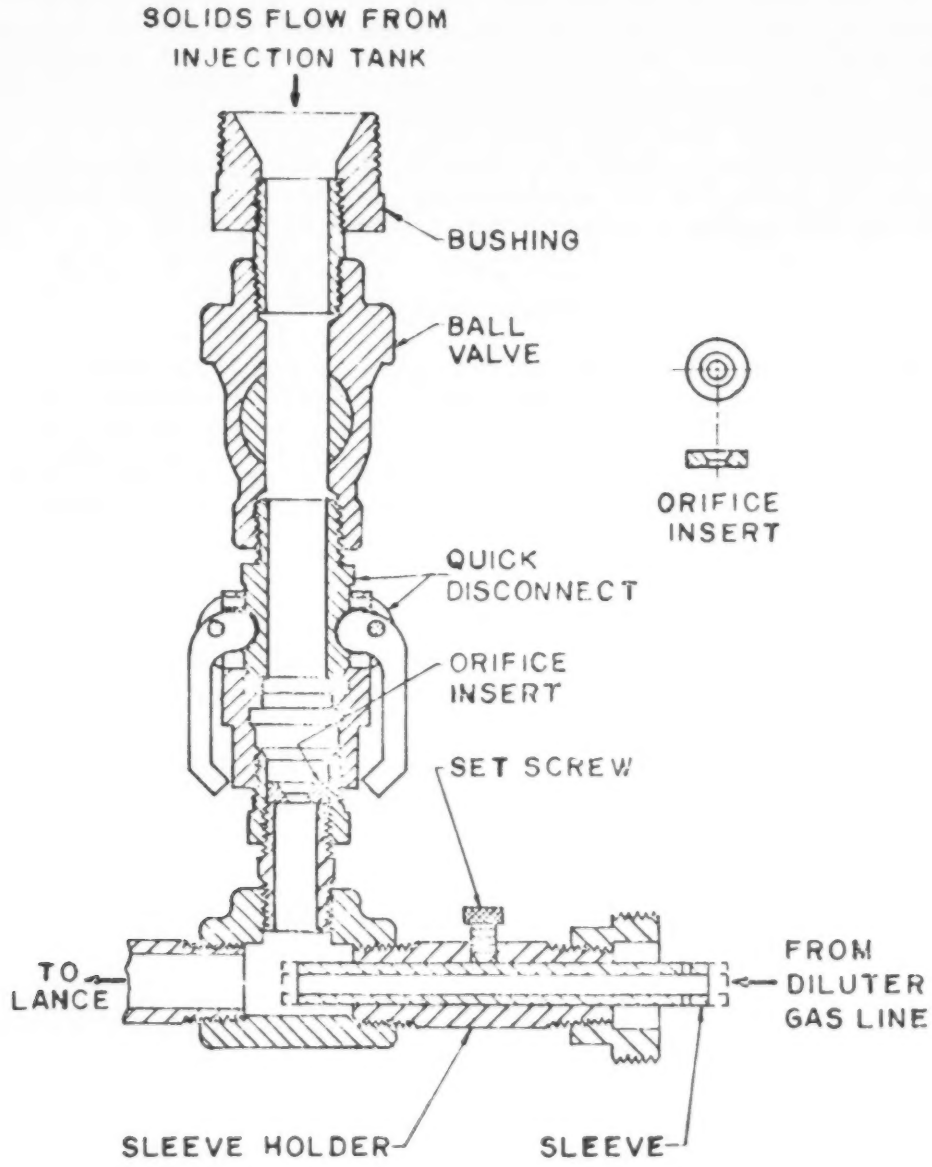

Fig. 31. Cross Section of Mixing Valve Assembly

Runs were made with as-received -14 mesh coal (moisture content of 4.0 wt %), and orifice diameters of 3/16, 1/4, and 5/16 in. In the run with a 3/16-in. orifice, the coal did not flow under various operating conditions. With a 1/4-in. orifice, coal flowed only for a short time (8.3 min) before plugging. With a 5/16-in. orifice, the average feed rate of coal was 136.9 lb/hr at an air flowrate of 1.4 scfm. Thus, for flow of as-received -14 mesh coal in the modified-standard Model 16 ABC Petrocarb Injector, an orifice having a diameter of 5/16 in. or larger must be used.

In runs with a longer transport line, lower feed rates could be achieved at a more uniform rate. The average feed rate for one run was as low as 22.2 lb/hr. One test was made with -14 mesh coal (containing 1.2 wt % moisture) and a 50-ft long tansport line. In this run, feeding of coal was initially irregular and eventually stopped.

Results of these exploratory tests showed that the feeder was not suitable for feeding at the rates required for the pressurized combustion unit tests and instead a rotary pocket feeder will be used.

VI. ACKNOWLEDGMENTS

We gratefully acknowledge the help given by Dr. R. C. Vogel, Mr. D. S. Webster, Dr. S. Lawroski, and Mr. L. Link in directing and reviewing the program, by Dr. S. Wood for his advice and assistance in equilibrium calculations, by the analysis team of Mr. M. Homa, Mrs. C. Blogg, Miss F. Ferry, Miss J. Williams, and Mr. Z. Tomczuk directed by Dr. R. Larsen and Mr. E. Kucera, and by our secretary, Miss P. Wood.

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